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Thesis
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THE CALCULATION OF ENTHALPY-ENTROPY DIAGRAM
FOR ROCKET PROPELLANT SYSTEMS

Thesis by

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ABSTRACT

The purpose of this thesis is to present a method and the fundamental data necessary to construct enthalpy-entropy diagrams and from these diagrams to calculate theoretical performance of rocket motor propellants. The systems investigated using this method are:

- (1) RFNA-Ammonia (1)
- (2) Ammonia (1)-Ozone (1)
- (3) Hydrogen (1)-Ozone (1)

Enthalpy-entropy diagrams for these fuels were constructed for several different mixture ratios: over-oxidized, stoichiometric, and under-oxidized. Performance was calculated assuming chamber pressures of 600 psia and 300 psia and exhaust pressures of 14.7 psia, 7.35 psia, and 0.147 psia. These diagrams facilitate the investigation of the effect of varying chamber pressure on chamber temperature and performance. They also facilitate investigation of varying expansion ratio, varying mixtures ratios, etc. They are especially useful in determining the performance of step rockets where exhaust conditions may vary from sea level to vacuum.

The results of the performance calculations indicate that performance found by using enthalpy-entropy diagrams check closely with those determined by other methods. The performance of the last two systems is such as to indicate that a more thorough study of them should be made.

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INTRODUCTION

The preparation of enthalpy-entropy diagrams starts logically with component calculations for the products of combustion in chemical equilibrium at selected temperatures and pressures. These components are used to calculate enthalpy and entropy points for the temperatures and pressures selected. The points are then plotted as enthalpy versus entropy for constant pressure to give the H-S diagrams.

It is natural to select a chamber pressure of 300 psia and an exhaust pressure of 14.7 psia since these conditions are universally used in comparing the performance of rocket propellants. Other values of chamber pressure and exhaust pressure may be used as desired. Temperatures which bracket the theoretical chamber and exhaust temperatures must be selected as well as any others that may be necessary to complete the diagrams.

An enthalpy-entropy diagram may be constructed assuming complete equilibrium for the products of combustion throughout the cycle, frozen equilibrium at combustion conditions, or any intermediate extent of reaction between these two conditions. In the body of this thesis complete equilibrium throughout the cycle is assumed. Performance based on frozen equilibrium is included in the appendix.

EXPLANATION OF SYMBOLS

- a Number of moles of hydrogen (H_2) in the products of reaction.
- b Number of moles of water vapor (H_2O) in the products of reaction.
- c Number of moles of carbon monoxide (CO) in the products of reaction.
- d Number of moles of carbon dioxide (CO_2) in the products of reaction.
- e Number of moles of oxygen (O_2) in the products of reaction.
- f Number of moles of nitrogen (N_2) in the products of reaction.
- g Number of moles of nitrous^{ic} oxide (NO) in the products of reaction.
- h Number of moles of hydroxyl ions (OH) in the products of reaction.
- i Number of moles of atomic hydrogen (H) in the products of reaction.
- j Number of moles of atomic oxygen (O) in the products of reaction.
- C Number of gram atoms of carbon in the reactants.
- H Number of gram atoms of hydrogen in the reactants.
- N Number of gram atoms of nitrogen in the reactants.
- O Number of gram atoms of oxygen in the reactants.
- K_n Equilibrium constant based on the ratio of the number of moles.

K_p	Equilibrium constant based on the partial pressures.
K_1	Particular equilibrium constant based on the ratios of the number of moles of component gases in given reactions.
x	Arbitrary constant defined by $\frac{K_{10}}{a}$
y	Arbitrary constant defined by $\frac{2K_6b}{a^2}$
z	Arbitrary constant defined by $\frac{K_7}{a}$
A	Arbitrary constant defined by $1 + x + y + z$ which is equal to $1 + \frac{K_{10}}{a} + \frac{2K_6b}{a^2} + \frac{K_7}{a}$
B	Arbitrary constant defined by $\frac{2g^2a^2}{K_3^2b^2} + g$
F	Arbitrary constant defined by $\frac{2g^2a^2}{K_3^2b^2} + g - N$
$n^{T^\circ K}$	Number of moles of products of reaction at temperature $T^\circ K$.
T_c	Equilibrium chamber temperature ($^\circ K$).
T_e	Exhaust temperature ($^\circ K$)
$\Delta H_{300^\circ K}^{T^\circ K}$	Enthalpy change between equilibrium temperature $T^\circ K$ and $300^\circ K$.
$\Delta H_{T_e}^{T_c}$	Enthalpy change between combustion chamber conditions and exit conditions.
R	Universal gas constant = 1.986 cal/gr. mole $^\circ K$.

Q_f	Heat of formation in kcal/mole at 300°K.
$Q_{av}^{T^{\circ}K}$	Heat available in kcal/mole at T°K from heat of chemical reaction.
P_c	Chamber pressure in psia.
P_e	Exhaust pressure in psia.
r	Mixture ratio; the ratio of the weight of oxidizer to weight of fuel in the propellant system.
J	Mechanical equivalent of heat = 4.186×10^{10} ergs/kcal.
V_c	Velocity of gases in the chamber.
c	Effective exhaust velocity in ft/sec.
I_{sp}	Specific impulse in lb-sec/lb.
g	Acceleration due to gravity - 32.16 ft/sec ² .
RFNA	Red Fuming Nitric Acid (in this thesis, nitric acid with 6.8% NO ₂)
$S_{T^{\circ}K}^{\circ}$	Absolute entropy in cal/mole °K.
Δh	Enthalpy change in kcal/gram
s°	Absolute entropy in cal/gram °K.

PART I

ASSUMPTIONS

The assumptions made in this thesis can be roughly grouped into two categories namely those concerning the thermodynamic properties of the gases and those concerning the expansion through the nozzle. For the former these assumptions are:

1. The values of enthalpy, entropy, and equilibrium constants used in this calculation are the best values available. In the compilation of these tables all internal energy states plus anharmonicities were considered. Imperfections due to attraction between molecules were not considered.
2. The temperature is such that the amount of atomic nitrogen present in the combustion products may be neglected. Previous investigations have shown this to be acceptable.
3. The values of Q_{av} and $\Delta H_{300^{\circ}K}^{T^{\circ}K}$ are linear within 100 degree intervals.
4. The datum for the enthalpy of a given species is zero at $300^{\circ}K$, and the entropy represents the absolute entropy of the pure perfect gas at a temperature of $T^{\circ}K$ and a pressure of one atmosphere.
5. The gases are perfect gases so that enthalpy is a function of composition and temperature only and not a function of pressure. This also implies that the

enthalpy of mixing may be neglected. If enthalpy is not a function of pressure, then the value of enthalpy of mixing is essentially zero for all cases now known.

6. The equipartition of energy among the electronic, vibrational, and rotational energy levels is assumed to be instantaneous both in the chamber and in the expansion process for both constant composition flow and equilibrium flow.

The assumptions for the nozzle are:

1. It is assumed in this thesis that the products of combustion are in the chamber a sufficient length of time to react completely and reach chemical equilibrium; and that equilibrium is maintained throughout the expansion so that when the gases reach the exhaust temperature and pressure, they have an equilibrium composition corresponding to that condition. The first assumption regarding equilibrium in the chamber is probably not too far wrong, but the second may be subjected to considerable criticism. During the expansion process the gases undergo a rapid change in temperature and pressure so that equilibrium may not be maintained at exhaust conditions. Perhaps the composition of the combustion gases is nearer the frozen composition or somewhere between the two extremes.

2. The expansion is isentropic. The flow is frictionless and shock-free.
3. The velocity of the gases in the combustion chamber (V_c) is negligible with respect to the exhaust velocity.
4. The nozzle is correctly designed for all exhaust conditions; the gases are expanded to atmospheric pressure in all cases.
5. The chamber pressures used are 600 psia and 300 psia. The exhaust pressures are 14.7 psia, 7.35 psia, and 0.147 psia.
6. The flow is assumed to be steady and non-viscous with a flat velocity profile radially.
7. The gravity effects may be neglected.

One of the advantages of this type of performance calculations is that it is not necessary to use an average value of the ratio of specific heats. Nor is it necessary to assume a constant one based on chamber conditions to determine exhaust temperature.

COMPONENT CALCULATIONS

The most tedious part of performance calculations is the solution for the components of the products of combustion at high temperatures. The equilibrium composition of a gaseous mixture is determined by the simultaneous equations of conservation of atomic species and of mass action. The scheme used in this calculation to permit one to solve for the components present in a system containing carbon, oxygen, hydrogen, and nitrogen is that developed by Dr. David Altman and Dr. Sidney Weinbaum of the Jet Propulsion Laboratory (Cf. Ref. 1).

For a system containing carbon, oxygen, hydrogen, and nitrogen, these equations are:

$$b = \frac{H - 2a - K_9 a^{\frac{1}{2}}}{2 + \frac{K_7 O}{a^2}} \quad (1)$$

$$g = 0 - C \left[\frac{K_1 a + 2b}{K_1 a + b} \right] - b \left[1 + \frac{K_7 O}{a^2} + \frac{K_7}{a} \right] - 2K_6 \frac{b^2}{a^2} \quad (2)$$

$$\frac{2 g^2 a^2}{K_3^2 b^2} + g - N = 0 = F(I) \quad (3)$$

$$d = \frac{b C}{b + K_1 a} \quad (4)$$

$$e = \frac{b^2}{a^2} K_6 \quad (5)$$

$$f = \frac{1}{2} (N-g) \quad (6)$$

$$h = \frac{b}{a^{\frac{1}{2}}} K_{10} \quad (7)$$

$$i = a^{\frac{1}{2}} K_9 \quad (8)$$

$$j = \frac{b}{a} K_7 \quad (9)$$

An explanation of the symbols used is made on page 2.

The procedure is as follows:

- (1) Choose a likely value of $a = n_{H_2}$
- (2) Calculate the corresponding value of b from equation (1).
- (3) Calculate the corresponding value of g from equation (2).
- (4) Substitute the values of a , b , and g into equation (3).
- (5) Repeat these steps and interpolate until the values of a , b , and c obtained make $F(I) = 0$.

In general, it will be found that if $F(I) > 0$, a should be decreased; and if $F(I) < 0$, a should be increased. A sample calculation is carried out below.

The equations used when one or more of the elements (C, H, N, or O) is missing, are listed below:

Case A: Systems containing only N, H, and O (C = zero)

$$b = \frac{H - 2a - K_9 a^{\frac{1}{2}}}{2 + \frac{K_{10}}{a^{\frac{1}{2}}}} \quad (1)$$

$$E = 0 - b \left[1 + \frac{K_{10}}{a^{\frac{1}{2}}} + \frac{K_7}{a} + \frac{2K_6 b}{a^2} \right] \quad (2)$$

$$\frac{2g^2 a^2}{K_3^2 b^2} + g - N - F(II) = 0 \quad (3)$$

Case B: Systems containing only C, H, and O (N=zero)

$$b = \frac{H - 2a - K_9 a^{\frac{1}{2}}}{2 + \frac{K_{10}}{a^{\frac{1}{2}}}} \quad (1)$$

$$b \left[1 + \frac{K_{10}}{a^{\frac{1}{2}}} + \frac{K_7}{a} + \frac{2K_6 b}{a^2} \right] + c \left[\frac{K_1 a + 2b}{K_1 a + b} \right] - 0 = F(III) = 0 \quad (2)$$

The proper a will make F(III) = 0.

Case C: Systems containing only H and O (C=N= zero).

$$b = \frac{H - 2a - K_9 a^{\frac{1}{2}}}{2 + \frac{K_{10}}{a^{\frac{1}{2}}}} \quad (1)$$

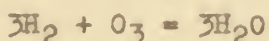
$$b \left[1 + \frac{K_{10}}{a^2} + \frac{K_7}{a} + \frac{2K_6b}{a^2} \right] - 0 = F(IV) = 0 \quad (2)$$

SAMPLE CALCULATION

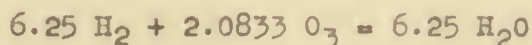
STOICHIOMETRIC MIXTURE OF $H_2(l)-O_2(l)$

To illustrate this method of calculating minor components a sample calculation is presented below. This calculation is carried out in greater detail on sample forms suitable for this computation in Tables VI and VII.

For the H_2-O_3 system the balanced equation at a stoichiometric mixture ratio when no minor components are considered is:



When an arbitrary basis of 100 grams of O_3 is selected this equation becomes:



The reactants now represent a combined weight of 112.6 grams and the number of atoms are:

$$H = 12.50$$

$$O = 6.25$$

The values of K in the component equations above are given in terms of the number of moles of the constituents and are related to the values of K_p (in terms of pressures) by the

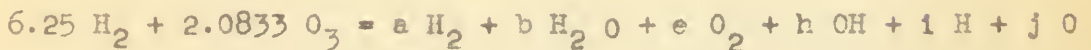
relation:

$$K = K_p (n/P)^{n_p - n_R}$$

where n = total number of moles
P = total pressure in atmospheres
 $n_p - n_R$ = difference in number of moles between the products and reactants for the particular reaction under consideration.

The values of K_p are given in Table I.

Assuming the chamber temperature to be 3000°K and the chamber pressure to be 300 psia (20.408 ^{atm}.) the balanced equation considering minor components becomes:



Since the system contains only O and H the equations used to solve for minor components are those listed in Case C above.

The total number of moles is estimated to be 6.63. This is based on a knowledge of the number of moles formed in the balanced equation with no minor components plus a knowledge of tendencies gained from previous experience. For the calculation of K_n in terms of the moles the following procedure is used:

$$n/P = \frac{6.63}{20.408} = .3249$$

$$(n/P)^{\frac{1}{2}} = (.3249)^{\frac{1}{2}} = .5700$$

$$K_6 = K_{p6}(n/P) = 0.001983 \times .3249 = .0006443$$

$$K_7 = K_{p7}(n/P) = 0.005336 \times .3249 = .001734$$

$$K_9 = K_{p9}(n/P)^{\frac{1}{2}} = 0.1579 \times .5700 = .09000$$

$$K_{10} = K_{p10}(n/P)^{\frac{1}{2}} = 0.0529 \times .5700 = .03015$$

Now, assuming a to be 0.42, solve for b using equation (1). b is found to be 5.6690. Putting these values of a and b into equation (2) yields $F = .0595$. It is apparent that a is too high, so a new value of $a = 0.40$ is selected and the calculations again carried out. This continued until F is as near zero as accuracy permits. Then all of the components can be found using equations (4) to (9) above.

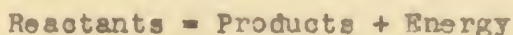
For the first case, after all of the components had been determined it was found that the total number of moles was 6.57 which differs from the first assumption of 6.63 moles. A new value of $n = 6.57$ is now assumed and the components recalculated. A similar procedure is carried out until the calculated number of moles equals the assumed number. These calculations are carried out in detail in Table VI.

The components were found to be:

a (H_2)	=	.396
b (H_2O)	=	5.690
c (O_2)	=	.132
h (OH)	=	.271
i (H)	=	.057
j (O)	=	.025

CHAMBER TEMPERATURE

To find the chamber temperature, it is necessary to select temperatures for component calculations which bracket the theoretical chamber temperature. According to the chemical equation expressing the change which occurs in the propellant:



The energy liberated in the reaction is called the heat available (Q_{av}) and is given by the relation:

$$Q_{av} = \sum n_i Q_{f_i} (\text{products}) - \sum n_i Q_{f_i} (\text{reactants})$$

where Q_{f_i} = heat of formation of i^{th} component in its specified state

n_i = i^{th} component

The value $\Delta H_{300^\circ\text{K}}^{T^\circ\text{K}}$ (the change of enthalpy from 300°K to $T^\circ\text{K}$) can be found in Table II.

The value $\Delta H_{300^\circ}^{T^\circ\text{K}}$ is given by:

$$\Delta H_{300^\circ}^{T^\circ\text{K}} = \sum n_i \Delta H_i$$

where n_i = the i^{th} component

$\Delta H_i = \Delta H_{300^\circ}^{T^\circ\text{K}}$ for the i^{th} component.

The actual chamber temperature is found by balancing the heat available to the change in enthalpy. Table II is based on setting the enthalpy at 300°K equal to zero, and the values of heats of formation used are based on the same temperature.

Therefore in this case, the balance is between $\Delta H_{300^\circ\text{K}}^{T_c}$ and $Q_{av}^{T_c}$. In actual practice the values of $\Delta H_{300^\circ\text{K}}^{T_c}$ and Q_{av} are assumed to be linear within 100° intervals.

For the sample calculation T_c was found to be between 3600°K and 3700°K .

For 3600°K

$$\Delta H_{300^\circ\text{K}}^{3600^\circ\text{K}} = 246.107 \text{ kcal/112.6 grams}$$

$$Q_{av}^{3600^\circ\text{K}} = 262.703 \text{ kcal/112.6 grams}$$

For 3700°K

$$\Delta H_{300^\circ\text{K}}^{3700^\circ\text{K}} = 256.106 \text{ kcal/112.6 grams}$$

$$Q_{av}^{3700^\circ\text{K}} = 230.949 \text{ kcal/112.6 grams}$$

By linear interpolation, $T_c = 3640^\circ\text{K}$.

ENTHALPY CALCULATIONS

The total enthalpy of a perfect gaseous mixture at $T^{\circ}\text{K}$ relative to its equilibrium composition at 300°K is:

$$\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}} = \sum (n_1^{300^{\circ}\text{K}} - n_1^{T^{\circ}\text{K}}) Q_{f_1} + \sum n_1^{T^{\circ}\text{K}} (\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}})_1$$

where $n_1^{300^{\circ}\text{K}}$ = number of moles of the i^{th} component at 300°K
 $n_1^{T^{\circ}\text{K}}$ = number of moles of the i^{th} component at $T^{\circ}\text{K}$.
 Q_{f_1} = heat of formation of the i^{th} component based on 300°K as given in Table IV (kcal/mole)
 $(\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}})_1$ = change in enthalpy of the i^{th} component between 300°K and $T^{\circ}\text{K}$ as given in Table II (kcal/mole)

The first term on the right hand side represents the heat of dissociation put in at 300°K to obtain the equilibrium composition at $T^{\circ}\text{K}$ and the second term represents the change of enthalpy due to heating the gas from 300°K to $T^{\circ}\text{K}$.

SAMPLE ENTHALPY CALCULATION

$$T = 3000^{\circ}\text{K}$$

$$n_1^{300^{\circ}\text{K}} \quad n_1^{T^{\circ}\text{K}} \quad (n_1^{300^{\circ}\text{K}} - n_1^{T^{\circ}\text{K}}) \quad Q_{f_1} \quad (n_1^{300^{\circ}\text{K}} - n_1^{T^{\circ}\text{K}}) \quad Q_{f_1}$$

(a) H_2	0.0	0.396	-0.396	0.0	0.0
(b) H_2O	6.25	5.690	+0.560	+57.798	+32.457
(e) O_2	0.0	0.132	-0.132	0.0	0.0
(h) OH	0.0	0.271	-0.271	-10.06	+2.726
(i) H	0.0	0.057	-0.057	-52.089	+2.969
(j) O	0.0	0.025	-0.025	-59.159	+1.479

$$\sum (n_1^{300^{\circ}\text{K}} - n_1^{T^{\circ}\text{K}}) Q_{f_1} = 39.541 \text{ kcal}$$

$$n_1^{T^{\circ}\text{K}} \quad (\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}})_1 \quad n_1^{T^{\circ}\text{K}} \quad (\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}})_1$$

(a) H_2	0.396	21.160	8.379
(b) H_2O	5.690	30.315	172.492
(e) O_2	0.132	23.427	3.092
(h) OH	0.271	21.447	5.812
(i) H	0.057	13.411	0.765
(j) O	0.025	13.411	0.336

$$\sum n_1^{T^{\circ}\text{K}} (\Delta H_{300^{\circ}\text{K}}^{T^{\circ}\text{K}})_1 = 190.876 \text{ kcal}$$

$$\sum (n_1^{300^\circ\text{K}} - n_1^{T^\circ\text{K}}) Q_{f_1} = 39.541 \text{ kcal}$$

$$\sum (n_1^{T^\circ\text{K}} (\Delta H_{300^\circ\text{K}}^{T^\circ\text{K}})_1 = \underline{190.876} \text{ kcal}$$

$$\Delta H_{300^\circ\text{K}}^{T^\circ\text{K}} = 230.417 \text{ kcal}$$

$$\Delta h = \frac{\Delta H}{m} = \frac{230.417 \text{ kcal}}{112.600 \text{ grams}} = 2.04633 \text{ kcal/gram}$$

This calculation is carried out in Table VII.

ENTROPY CALCULATION

The entropy of a perfect gas composed of several components at temperature $T^{\circ}K$ is given by:

$$S_{T^{\circ}K}^{\circ} = \sum_i^{T^{\circ}K} (S_{T^{\circ}K}^{\circ})_i - n^{T^{\circ}K} R \ln P - \sum_i^{T^{\circ}K} n_i^{T^{\circ}K} R \ln \frac{n_i^{T^{\circ}K}}{n}$$

where $S_{T^{\circ}K}^{\circ}$ = absolute entropy at $T^{\circ}K$ in cal/degree.

$n_i^{T^{\circ}K}$ = number of moles of the i^{th} component at $T^{\circ}K$.

$(S_{T^{\circ}K}^{\circ})_i$ absolute entropy of the i^{th} component in cal/degree/mole as given in Table III.

$n^{T^{\circ}K}$ = total number of moles of products of combustion at $T^{\circ}K$.

R = Universal gas constant = 1.986 cal/degree/mole.

P = Chamber pressure in atmospheres.

The first term on the right hand side represents the absolute entropy at $T^{\circ}K$. The second term represents the correction to the absolute entropy due to the total pressure of the gases. The third term represents the change in entropy due to the mixing of the several component gases. Fundamentally, it represents the terms $\sum_i^{T^{\circ}K} n_i^{T^{\circ}K} R \ln (\text{Probability})$ where the probability of finding the i^{th} component in this case is

$n_1^{T^0K}/n^{T^0K}$. The entropy of mixing is therefore $\sum n_i^T R \ln \frac{n_1^{T^0K}}{n^{T^0K}}$

Another way to look at the second and third terms is when combined, they become the change of entropy due to the partial pressure of each component

$$\sum n_i R \ln P + \sum n_i R \ln \frac{n_i}{n} = \sum n_i R \ln \frac{n_i P}{n} = \sum n_i R \ln P_i$$

where P_i = partial pressure of the i^{th} component so that the entropy of mixing contains the correction due to the use of total pressure instead of partial pressure of each component.

SAMPLE ENTROPY CALCULATION

$$T = 3000^{\circ}\text{K}$$

	$n_1^{3000^{\circ}\text{K}}$	$(s_{3000^{\circ}\text{K}}^{\circ})_1$	$n_1^{3000^{\circ}\text{K}}(s_{3000^{\circ}\text{K}}^{\circ})_1$
(a) H_2	.396	48.47	19.194
(b) H_2O	5.690	68.14	387.717
(c) O_2	.132	67.95	8.969
(h) OH	.271	61.39	16.637
(i) H	.057	38.81	2.212
(j) O	.025	49.47	1.237

$$\sum n_1^{3000^{\circ}\text{K}}(s_{3000^{\circ}\text{K}}^{\circ})_1 = 435.966 \text{ cal/deg}$$

$$n R \ln P = 6.571 \times 1.986 \times \ln 20.408 = 39.353 \text{ cal/deg}$$

	$n_1^{3000^{\circ}\text{K}}$	$n_1^{3000^{\circ}\text{K}}/n^{3000^{\circ}\text{K}}$	$\ln n_1/n$	$n_1 \ln n_1/n$
(a) H_2	.396	.06027	2.8084	1.112
(b) H_2O	5.690	.86606	.1438	.818
(c) O_2	.132	.02009	3.9070	.516
(h) OH	.271	.04125	3.1893	.864
(i) H	.057	.00852	4.7677	.272
(j) O	.025	.00381	5.5728	.139

$$\sum n_1 \ln n_1/n = 3.717 \text{ moles}$$

$$\sum n_1 R \ln \frac{n_1}{n} = 3.717 \times 1.986 = 7.382 \text{ cal/deg}$$

SUMMARY

$$\sum n_1^T (s_{3000^\circ K}^0)_1 = + 435.966 \quad \text{cal/deg}$$

$$- n R \ln 20.408 = - 39.353 \quad \text{cal/deg}$$

$$-\sum n_1^T R \ln \frac{n_1^T}{n} = + \underline{7.382} \quad \text{cal/deg}$$

$$s_{3000^\circ K}^0 = 403.995 \quad \text{cal/deg}$$

$$s^0 = \frac{403.995}{112.6} = 3.58788 \quad \text{cal/deg/gram}$$

These calculations are also carried out in Table VII.

PART II

THEORY AND USE OF H-S DIAGRAM

The fundamental process used in all jet propulsion motors is the conversion of heat energy into kinetic energy by an adiabatic expansion process. The basic equation is:

$$\Delta H + \frac{\Delta(v^2)}{2gJ} + \frac{\Delta Z}{J} = q - w_s \quad (1)$$

where ΔH = increase in enthalpy/unit wt of the fluid

$\frac{\Delta(v^2)}{2gJ}$ = increase in kinetic energy/unit of wt. of the fluid

$\frac{\Delta Z}{J}$ = increase in potential energy/unit wt. of the fluid

q = heat added to the system/unit wt. of the fluid

w_s = work done by the system/unit wt. of the fluid

It is assumed that the change of potential energy, heat added, and work done are zero, so the equation for a rocket becomes:

$$\Delta H + \frac{\Delta(v^2)}{2gJ} = 0 \quad (2)$$

In the combustion chamber the velocity is assumed to be negligible when compared to the jet velocity so;

$$\Delta(v^2) = v_c^2 - c^2 = -c^2$$

where V_c = velocity of the gases in the chamber which is assumed to be zero

c = effective exhaust velocity

Thus the equation for the exhaust velocity becomes:

$$c = (2g J \Delta H)^{\frac{1}{2}}$$

where the units are consistent. When the equation is reduced to a convenient form it becomes:

$$c = 0.03281 \left(\frac{2 \Delta H_{T_e}^{T_c} J}{m} \right)^{\frac{1}{2}}$$

where J = mechanical equivalent of heat = $4.816 \times 10^{10} \frac{\text{ergs}}{\text{kcal}}$

0.03281 converts cm/sec to ft/sec.

The value of $\Delta H_{T_e}^{T_c}$ can be read directly from the enthalpy-entropy charts. This is illustrated in Figure 18. Enter with $\Delta h = \frac{\Delta H_{300^\circ K}^{T_c^\circ K}}{m}$ corresponding to the chamber conditions

and expand isentropically to the exhaust conditions. The results for the systems investigated are tabulated in Table IX.

After solving for c it is easy to determine I_{sp} which is defined as:

$$I_{sp} = c/g$$

Where g = acceleration due to gravity - 32.16 ft/sec^2 .

The values of I_{sp} for the systems investigated are also tabulated in Table IX.

Another type of diagram that may be constructed from this data is temperature versus entropy for lines of constant pressure. From this diagram exit temperatures may be read directly.

PART III

RESULTS AND CONCLUSIONS

As far as it has been possible to determine, the performance calculated by this method agrees closely with that determined by other methods. This method has an advantage in that the errors introduced by using an average value of the ratio of the specific heats to calculate exhaust temperatures and the use of an average molecular weight resulting from composition changes are eliminated.

These diagrams are especially useful in evaluating the performance of rocket fuels with varying chamber and exhaust conditions. It is very easy to rapidly determine I_{sp} for different exhaust pressures. It is also easy to compare performances that might be obtained by varying conditions.

The labor in evaluating one set of conditions is considerably greater for the H-S diagram than for other methods; but for a comprehensive study of system, the labor is not much different. If one or only a few propellant combinations are finally selected as optimum, it will be very beneficial to construct enthalpy-entropy diagrams for those systems.

Using this method it is easy to consider efficiencies, heat transfer, and changes of entropy.

The results of these calculations show that the propellants $NH_3(l) - O_3(l)$ and $H_2(l) - O_3(l)$ are high performance propellants but they have high temperatures as well.

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Table
Equilibrium constants.

Temp. (°K)	K ₁	K ₂	K ₃	K ₄	K ₅	K ₆	K ₇	K ₈	K ₁₀
296.1	1 007 x 10 ⁻⁵	7 82 x 10 ⁻²⁴		7 280 x 10 ²	1 58 x 10 ⁻²⁴				
700	0 1110	3 637 x 10 ⁻³		9 150 x 10 ⁻³	1 06 x 10 ⁻¹³				
800	2478	31 25		2 909 x 10 ⁻³	9 84 x 10 ⁻¹¹				
900	4546	0 7513		1 177 x 10 ⁻⁴	1 46 x 10 ⁻¹¹				
1000	7286	03720		5 636 x 10 ⁻⁴	3 29 x 10 ⁻¹⁰				
1100	1 056	3 147 x 10 ⁻³		3 070 x 10 ⁻⁴	9 55 x 10 ⁻⁹				
1200	1 435	3 994 x 10 ⁻⁴		1 647 x 10 ⁻⁴	3 39 x 10 ⁻⁸				
1300	1 644	6 975 x 10 ⁻⁵		1 166 x 10 ⁻⁴	1 40 x 10 ⁻⁸				
1400	2 270	1 553 x 10 ⁻⁵		6 239 x 10 ⁻⁵	6 56 x 10 ⁻⁸				
1500	2 704	4 216 x 10 ⁻⁶		5 946 x 10 ⁻⁵	3 36 x 10 ⁻⁸				
1600	3 135	1 348 x 10 ⁻⁶		4 486 x 10 ⁻⁵	1 69 x 10 ⁻⁸				
1700	3 555	4 925 x 10 ⁻⁷		3 478 x 10 ⁻⁵	1 13 x 10 ⁻⁸				
1800	3 975	2 029 x 10 ⁻⁷		2 783 x 10 ⁻⁵	7 04 x 10 ⁻⁹				
1900	4 393	9 211 x 10 ⁻⁸		2 293 x 10 ⁻⁵	4 66 x 10 ⁻⁹				
2000	4 782	4 545 x 10 ⁻⁸	5 734 x 10 ⁻⁶	1 923 x 10 ⁻⁵	3 19 x 10 ⁻⁹	8 13 x 10 ⁻⁶	2 08 x 10 ⁻⁶	1 629 x 10 ⁻³	1 644 x 10 ⁻⁴
2100	5 149	2 393 x 10 ⁻⁸	1 496 x 10 ⁻⁵	1 641 x 10 ⁻⁵	2 26 x 10 ⁻⁹	3 45 x 10 ⁻⁶	8 85 x 10 ⁻⁷	3 119 x 10 ⁻³	3 698 x 10 ⁻⁴
2200	5 420	1 320 x 10 ⁻⁸	6 69 x 10 ⁻⁵	1 421 x 10 ⁻⁵	1 65 x 10 ⁻⁹	1 308 x 10 ⁻⁶	3 34 x 10 ⁻⁶	5 810 x 10 ⁻³	6 072 x 10 ⁻⁴
2300	5 853	7 902 x 10 ⁻⁹	6 29 x 10 ⁻⁵	1 247 x 10 ⁻⁵	1 24 x 10 ⁻⁹	4 19 x 10 ⁻⁶	1 086 x 10 ⁻⁶	1 560 x 10 ⁻³	1 567 x 10 ⁻³
2400	6 140	4 873 x 10 ⁻⁹	1 689 x 10 ⁻⁴	1 107 x 10 ⁻⁵	9 48 x 10 ⁻⁹	1 260 x 10 ⁻⁶	3 305 x 10 ⁻⁵	1 592 x 10 ⁻²	2 951 x 10 ⁻³
2500	6 440	3 138 x 10 ⁻⁹	3 512 x 10 ⁻⁴	9 95 x 10 ⁻⁶	7 40 x 10 ⁻⁹	3 452 x 10 ⁻⁶	9 121 x 10 ⁻⁵	2 514 x 10 ⁻²	5 230 x 10 ⁻³
2600	6 668	2 089 x 10 ⁻⁹	6 74 x 10 ⁻⁴	9 00 x 10 ⁻⁶	3 69 x 10 ⁻⁹	8 65 x 10 ⁻⁶	2 34 x 10 ⁻⁵	3 357 x 10 ⁻²	6 995 x 10 ⁻³
2700	6 954	1 435 x 10 ⁻⁹	1 168 x 10 ⁻³	8 21 x 10 ⁻⁶	4 74 x 10 ⁻⁹	2 06 x 10 ⁻⁶	6 55 x 10 ⁻⁵	5 675 x 10 ⁻²	1 462 x 10 ⁻²
2800	7 185	1 016 x 10 ⁻⁹	2 05 x 10 ⁻³	7 56 x 10 ⁻⁶	3 97 x 10 ⁻⁹	4 64 x 10 ⁻⁶	1 243 x 10 ⁻⁴	6 185 x 10 ⁻¹	2 312 x 10 ⁻²
2900	7 376	7 360 x 10 ⁻¹⁰	3 42 x 10 ⁻³	6 88 x 10 ⁻⁶	3 21 x 10 ⁻⁹	9 60 x 10 ⁻⁶	2 65 x 10 ⁻³	1 146 x 10 ⁻¹	3 556 x 10 ⁻²
3000	7 562	5 456 x 10 ⁻¹⁰	5 479 x 10 ⁻³	6 49 x 10 ⁻⁶	2 69 x 10 ⁻⁹	1 963 x 10 ⁻⁶	5 336 x 10 ⁻³	0 1579	5 290 x 10 ⁻²
3100	7 746		8 525 x 10 ⁻³		2 37 x 10 ⁻⁹	3 803 x 10 ⁻⁶	1 027 x 10 ⁻²	2 125	7 677 x 10 ⁻²
3200	7 929		1 284 x 10 ⁻²		1 94 x 10 ⁻⁹	7 055 x 10 ⁻⁶	1 904 x 10 ⁻²	2613	1 087 x 10 ⁻¹
3300	8 078		1 859 x 10 ⁻²		1 66 x 10 ⁻⁹	1 248 x 10 ⁻⁶	3 389 x 10 ⁻²	3634	1 513 x 10 ⁻¹
3400	8 192		2 758 x 10 ⁻²		1 44 x 10 ⁻⁹	2 157 x 10 ⁻⁶	5 857 x 10 ⁻²	4662	2 060 x 10 ⁻¹
3500	8 304	1 621 x 10 ⁻¹⁰	3 884 x 10 ⁻²	4 68 x 10 ⁻⁶	1 26 x 10 ⁻⁹	3 563 x 10 ⁻⁶	9 778 x 10 ⁻²	5910	2 763 x 10 ⁻¹
3600	8 449		5 404 x 10 ⁻²		1 10 x 10 ⁻⁹	5 821 x 10 ⁻⁶	1 591 x 10 ⁻¹	7347	8 644 x 10 ⁻¹
3700	8 538		7 355 x 10 ⁻²		9 69 x 10 ⁻⁹	8 66 x 10 ⁻⁶	2 516 x 10 ⁻¹	9044	4 691 x 10 ⁻¹
3800	8 664		9 821 x 10 ⁻²		6 59 x 10 ⁻⁹	1 412 x 10 ⁻⁵	3 876 x 10 ⁻¹	1 107	5 964 x 10 ⁻¹
3900	8 712		1 300 x 10 ⁻¹		7 64 x 10 ⁻⁹	2 134 x 10 ⁻⁵	5 678 x 10 ⁻¹	1 336	7 569 x 10 ⁻¹
4000	8 752	6 66 x 10 ⁻¹¹	1 693 x 10 ⁻¹	3 94 x 10 ⁻⁶	6 83 x 10 ⁻⁹	3 157 x 10 ⁻⁵	6 711 x 10 ⁻¹	1 597	9 495 x 10 ⁻¹
4100									
4200	8 819		2 162 x 10 ⁻¹		6 12 x 10 ⁻⁹	4 526 x 10 ⁻⁵	1 256	1 893	1 164
4300	8 864		2 760 x 10 ⁻¹		5 52 x 10 ⁻⁹	6 519 x 10 ⁻⁵	1 606	2 226	1 428
4400	8 898		3 463 x 10 ⁻¹		5 01 x 10 ⁻⁹	9 139 x 10 ⁻⁵	1 206 x 10 ⁻¹	2 596	1 730
4500	8 928		4 302 x 10 ⁻¹		4 51 x 10 ⁻⁹	1 263	3 508	3 012	2 089
4600	8 952	3 36 x 10 ⁻¹¹	5 291 x 10 ⁻¹	3 36 x 10 ⁻⁶	4 10 x 10 ⁻⁹	1 716	4 778	3 470	2 478
4700									
4800	8 974		6 451 x 10 ⁻¹		3 74 x 10 ⁻⁹	2 307	6 431	3 969	2 923
4900	8 984		7 798 x 10 ⁻¹		3 41 x 10 ⁻⁹	3 068	6 545	4 820	3 432
5000	8 994		6 344 x 10 ⁻¹		3 12 x 10 ⁻⁹	4 075	11 21	5 116	3 992
4900	9 003				2 66 x 10 ⁻⁹	6 226	14 59	5 764	4 637
5000	9 012	2 02 x 10 ⁻¹¹		3 00 x 10 ⁻⁶	2 63 x 10 ⁻⁹	6 693	18 77	6 461	5 317

- See next page for definitions of K₁, K₂

Table [Concluded.]

Temp. (°K)	K ₁₁	K ₁₂	K ₁₃	K ₁₄	K ₁₅	K ₁₆	K ₁₇
298.1							
400							3.976 × 10 ⁻⁵
500							1.822 × 10 ⁻⁵
600							1.026 × 10 ⁻⁵
700							6.660 × 10 ⁻⁶
800							4.724 × 10 ⁻⁶
900							3.603 × 10 ⁻⁶
1000							2.888 × 10 ⁻⁶
1100	2.11 × 10 ⁻¹⁰					2.22 × 10 ⁻¹⁵	2.416 × 10 ⁻⁶
1200							2.081 × 10 ⁻⁶
1300							1.835 × 10 ⁻⁶
1400							1.653 × 10 ⁻⁶
1500	2.98 × 10 ⁻¹¹				2.77 × 10 ⁻⁶	9.878 × 10 ⁻¹⁶	1.510 × 10 ⁻⁶
2000	1.13 × 10 ⁻¹¹				2.37 × 10 ⁻⁶	7.290 × 10 ⁻¹⁶	1.135 × 10 ⁻⁶
2500	6.62 × 10 ⁻¹²				2.23 × 10 ⁻⁶	7.446 × 10 ⁻¹⁶	9.87 × 10 ⁻⁷
3000		8.27 × 10 ⁻⁹	3.55 × 10 ⁻⁷	1.90 × 10 ⁻⁴	2.16 × 10 ⁻⁶		9.93 × 10 ⁻⁷
3500		3.80 × 10 ⁻⁷	8.49 × 10 ⁻⁷	7.61 × 10 ⁻⁴	2.16 × 10 ⁻⁶		9.89 × 10 ⁻⁷
4000		1.20 × 10 ⁻⁶	1.65 × 10 ⁻⁶	2.15 × 10 ⁻³	2.17 × 10 ⁻⁶		9.88 × 10 ⁻⁷
4500		2.92 × 10 ⁻⁶	2.62 × 10 ⁻⁶	4.80 × 10 ⁻³	2.22 × 10 ⁻⁶		9.87 × 10 ⁻⁷
5000		5.96 × 10 ⁻⁶	4.41 × 10 ⁻⁶	9.09 × 10 ⁻³	2.28 × 10 ⁻⁶		9.88 × 10 ⁻⁷

$$K_1 = P_{CO}P_{H_2O}/P_{CO_2}P_{H_2}; \quad K_2 = P_{CH_4}P_{H_2O}/P_{H_2}^2P_{CO}; \quad K_3 = P_{NO}P_{H_2}/P_{N_2}^{1/2}P_{H_2O};$$

$$K_4 = P_{NH_3}/P_{N_2}^{1/2}P_{H_2}^{3/2}; \quad K_5 = P_{CO}/P_{O_2}^{1/2}; \quad K_6 = P_{O_2}P_{H_2}^2/P_{H_2O}^2;$$

$$K_7 = P_{O}P_{H_2}/P_{H_2O}; \quad K_8 = P_N/P_{N_2}^{1/2}; \quad K_9 = P_H/P_{H_2}^{1/2}; \quad K_{10} = P_{OH}P_{H_2}^{1/2}/P_{H_2O};$$

$$K_{11} = P_{C_2H_2}P_{H_2O}^2/P_{CO}^2P_{H_2}^2; \quad K_{12} = P_{CH}P_{H_2O}/P_{CO}P_{H_2}^{3/2};$$

$$K_{13} = P_{CN}P_{CO_2}/P_{CO}^2P_{N_2}^{1/2}; \quad K_{14} = P_{NH}/P_{N_2}^{1/2}P_{H_2}^{3/2};$$

$$K_{15} = P_{HCN}P_{H_2O}/P_{CO}P_{H_2}^2P_{N_2}^{1/2}; \quad K_{16} = P_{C_2N_2}P_{CO_2}^2/P_{CO}^2P_{N_2};$$

$$K_{17} = P_{H_2CO}/P_{H_2}P_{CO}.$$

ENTHALPY TABLE
 $\Delta H_{300}^{T^{\circ}K}$ kcal./gram mole

T ^{°K}	H ₂	H ₂ O	CO	CO ₂	O ₂	N ₂	OH	NO	H,N,O	ΔT
300	0.0	0.0	0.0	0.0	0.0	0.0			0.0	0.0
400	0.695	0.811	0.899	0.942	0.721	0.897			0.497	0.199
500	1.393	1.641	1.404	1.970	1.447	1.399			0.993	0.397
600	2.093	2.496	2.125	3.072	2.203	2.112			1.490	0.596
700	2.796	3.360	2.862	4.232	2.981	2.840			1.987	0.795
800	3.502	4.292	3.615	5.441	3.778	3.582			2.484	0.993
900	4.212	5.234	4.386	6.692	4.594	4.343			2.981	1.192
1000	4.931	6.208	5.171	7.976	5.421	5.118	4.985	5.308	3.477	1.390
1100	5.657	7.211	5.973	9.291	6.278	5.907	5.725	6.133	3.974	1.589
1200	6.393	8.247	6.785	10.629	7.135	6.709	6.465	6.958	4.471	1.788
1300	7.138	9.312	7.606	11.989	7.990	7.520	7.233	7.800	4.967	1.986
1400	7.895	10.399	8.437	13.367	8.847	8.342	8.002	8.643	5.464	2.185
1500	8.664	11.519	9.275	14.760	9.704	9.173	8.783	9.499	5.961	2.384
1600	9.439	12.660	10.120	16.168	10.592	10.009	9.584	10.355	6.457	2.582
1700	10.226	13.821	10.972	17.587	11.481	10.854	10.390	11.221	6.954	2.781
1800	11.023	15.006	11.829	19.017	12.369	11.703	11.197	12.088	7.451	2.980
1900	11.828	16.206	12.689	20.455	13.257	12.558	12.015	12.957	7.947	3.178
2000	12.644	17.424	13.554	21.902	14.146	13.417	12.834	13.827	8.444	3.377
2100	13.468	18.659	14.423	23.358	15.061	14.279	13.643	14.700	8.941	3.576
2200	14.295	19.909	15.294	24.820	15.974	15.143	14.506	15.598	9.438	3.774
2300	15.132	21.171	16.169	26.290	16.889	16.013	15.360	16.480	9.935	3.973
2400	15.975	22.446	17.045	27.760	17.802	16.883	16.213	17.364	10.430	4.171
2500	16.827	23.733	17.923	29.242	18.717	17.758	17.080	18.249	10.928	4.370
2600	17.683	25.031	18.807	30.729	19.659	18.636	17.936	19.143	11.425	4.569
2700	18.542	26.338	19.691	32.218	20.601	19.516	18.807	20.036	11.921	4.767
2800	19.410	27.656	20.576	33.712	21.543	20.399	19.678	20.929	12.418	4.966
2900	20.282	28.980	21.464	35.211	22.488	21.284	20.563	21.823	12.915	5.165
3000	21.160	30.315	22.353	36.712	23.427	22.170	21.447	22.716	13.411	5.363
3100	22.041	31.658	23.242	38.222	24.384	23.058	22.335	23.617	13.908	5.562
3200	22.927	33.006	24.136	39.734	25.344	23.947	23.227	24.519	14.405	5.761
3300	23.818	34.362	25.028	41.244	26.308	24.837	24.121	25.421	14.901	5.959
3400	24.712	35.723	25.923	42.764	27.276	25.729	25.021	26.325	15.398	6.158
3500	25.611	37.092	26.818	44.281	28.247	26.622	25.920	27.229	15.894	6.356
3600	26.512	38.466	27.715	45.808	29.219	27.516	26.822	28.135	16.392	6.555
3700	27.416	39.845	28.613	47.332	30.198	28.412	27.730	29.041	16.889	6.754
3800	28.328	41.231	29.512	48.862	31.178	29.307	28.640	29.948	17.385	6.952
3900	29.236	42.619	30.412	50.394	32.164	30.205	29.552	30.856	17.882	7.151
4000	30.153	44.010	31.313	51.930	33.153	31.104	30.467	31.761	18.379	7.350
4100	31.069	45.413	32.215	53.471	34.139	32.006	31.390	32.682	18.875	7.548

SOURCE OF DATA:

*THERMODYNAMIC PROPERTIES OF PROPELLANT GASES, HIRSCHFELDER, CURTIS, MCCLURE, AND OSBORNE, O. S. R. D. REPORT # 547.

NOTE: FOR USE OF THIS TABLE IN CALCULATING THEORETICAL PROPELLANT PERFORMANCE
 Cf: PROGRESS REPORT 1.25

ENTROPY TABLE ($S_{T^{\circ}K}^{\circ}$)

(cal/degree/mole)

$T^{\circ}K$	H ₂ O	CO	CO ₂	O ₂	N ₂	NO	OH	H	N	O	h _c
300	44.80	47.30	50.20	49.00	45.80	50.40		27.40	36.62	38.06	21.27
400	47.12	49.31	52.89	51.06	47.79	52.45		28.82	38.04	39.48	33.27
500	43.96	50.38	55.17	52.67	49.35	54.06		29.92	39.14	40.58	34.83
600	50.52	52.19	57.17	54.05	50.65	55.40		30.82	40.04	41.48	36.10
700	51.88	53.32	58.96	55.25	51.77	56.57		31.59	40.81	42.25	37.18
800	53.10	54.32	60.57	56.31	52.76	57.60		32.25	41.47	42.91	38.12
900	54.21	55.23	62.04	57.27	53.66	58.53		32.84	42.06	43.50	38.96
1000	55.24	56.06	63.39	58.14	54.48	59.38	52.51	33.36	42.58	44.02	39.72
1100	56.20	56.82	64.64	58.96	55.23	60.17	53.21	33.83	43.05	44.49	40.41
1200	57.10	57.53	65.80	59.71	55.93	60.89	53.86	34.26	43.48	44.92	41.05
1300	57.95	58.19	66.89	60.39	56.58	61.56	54.47	34.66	43.88	45.32	41.65
1400	58.76	58.81	67.91	61.03	57.19	62.18	55.04	35.03	44.25	45.69	42.21
1500	59.53	59.39	68.87	61.62	57.76	62.77	55.58	35.37	44.59	46.03	42.74
1600	60.27	59.94	69.78	62.19	58.30	63.32	56.10	35.69	44.91	46.35	43.24
1700	60.97	60.46	70.64	62.73	58.81	63.85	56.58	35.99	45.21	46.65	43.72
1800	61.65	60.95	71.46	63.24	59.30	64.35	57.05	36.27	45.49	46.93	44.17
1900	62.30	61.42	72.24	63.72	59.76	64.82	57.49	36.54	45.76	47.20	44.61
2000	62.93	61.86	72.98	64.18	60.20	65.27	57.91	36.80	46.02	47.46	45.03
2100	63.53	62.28	73.69	64.63	60.62	65.70	58.30	37.04	46.26	47.70	45.43
2200	64.11	62.69	74.37	65.06	61.02	66.12	58.70	37.27	46.49	47.93	45.81
2300	64.67	63.08	75.02	65.47	61.41	66.51	59.08	37.49	46.71	48.15	46.19
2400	65.21	63.45	75.65	65.86	61.78	66.89	59.45	37.70	46.92	48.36	46.54
2500	65.74	63.81	76.26	66.23	62.14	67.25	59.80	37.90	47.12	48.56	46.89
2600	66.25	64.16	76.84	66.60	62.48	67.60	60.14	38.10	47.32	48.76	47.23
2700	66.74	64.49	77.40	66.96	62.81	67.94	60.47	38.29	47.51	48.95	47.55
2800	67.22	64.81	77.94	67.30	63.13	68.27	60.78	38.47	47.69	49.13	47.87
2900	67.69	65.12	78.47	67.63	63.44	68.58	61.09	38.64	47.86	49.30	48.17
3000	68.14	65.42	78.98	67.95	63.74	68.88	61.39	38.81	48.03	49.47	48.47
3100	68.58	65.71	79.48	68.26	64.03	69.18	61.68	33.97	48.19	49.63	48.76
3200	69.01	65.99	79.96	68.57	64.31	69.47	61.97	39.13	48.35	49.79	49.04
3300	69.43	66.26	80.43	68.87	64.58	69.75	62.24	39.28	48.50	49.94	49.32
3400	69.84	66.53	80.88	69.16	64.85	70.02	62.51	39.43	48.65	50.09	49.57
3500	70.24	66.79	81.32	69.44	65.11	70.28	62.77	39.57	48.79	50.23	49.84
3600	70.63	67.04	81.75	69.71	65.36	70.54	63.03	39.71	48.93	50.37	50.01
3700	71.01	67.29	82.17	69.98	65.61	70.79	63.28	39.85	49.07	50.51	50.34
3800	71.38	67.53	82.58	70.24	65.85	71.03	63.52	39.98	49.20	50.64	50.59
3900	71.74	67.76	82.98	70.50	66.08	71.27	63.76	40.11	49.33	50.77	50.82
4000	72.09	67.99	83.37	70.75	66.31	71.50	63.99	40.24	49.46	50.90	51.05
4100	72.44	68.21	83.75	70.99	66.53	71.73	64.22	40.36	49.58	51.02	51.28

TABLE IV

HEATS OF FORMATION AT CONSTANT PRESSURE
USED IN THIS ANALYSIS

<u>Constituent</u>	<u>Heat of Formation in Kilocalories per Mole</u>
H ₂ O	+57.798
NO	-21.600
OH	-10.060
H	-52.089
O	-59.159
NH ₃ (1)	+16.070
NO ₂	- 6.100
HNO ₃	+41.660
O ₃ (1)	-31.500
H ₂ (1)	+ 1.848

TABLE V

ATOMIC WEIGHTS USED

<u>Element</u>	<u>Atomic Weight</u>
N	14.008
H	1.008
O	16.000
H ₂	2.016
H ₂ O	34.016
NH ₃	17.032
HN ₃	63.016
NO ₂	46.008
O ₃	48.000

TABLE VI
SAMPLE CALCULATION SHEET (A)

H-12.50
O- 6.25
N-

$H_2 - O_3$

STOIC

P=300 PSIA
T=3000° K

	6.63			6.57				
Kn	3							
	6	.0006443		.0006383				
2K ₆	.0012886			.0012766				
	7	.001734		.001718				
	9	.09000		.08959				
	10	.03015		.03002				
a	.42	.40	.398	.398	.396			
2a	.84	.80	.796	.796	.792			
a ^{1/2}	.6481	.6325	.6309	.6309	.6293			
a ²	.1764	.1600	.1584	.1584	.1568			
x K ₁₀ /a ^{1/2}	.04652	.04767	.04779	.04758	.04770			
2+K ₁₀ /a ^{1/2}	2.04652	2.04767	2.04779	2.04758	2.04770			
K ₉ a ^{1/2}	.05833	.05693	.05678	.05652	.05638			
H-2a-K ₉ a ^{1/2}	11.6017	11.6431	11.6472	11.6474	11.6516			
b	5.6690	5.686	5.6877	5.6884	5.6901			
b ²	32.1376	32.3306	32.3499	32.3579	32.3772			
y 2K ₆ b/a ²	.04139	.04579	.04627	.04584	.04633			
z K ₇ /a	.004129	.004335	.004357	.004316	.004338			
A 1+k+y+z	1.0920	1.0978	1.0984	1.0977	1.0984			
bA	6.1905	6.2421	6.2475	6.2444	6.2500			
g								
g ²								
K ₃ ²								
B								
F	-.0595	-.0079	-.0025	-.0056	0.0			
a			.3980		.396			
b			5.6877		5.690			
e			.1316		.132			
f								
g								
h			.2718		.271			
i			.0568		.056			
j			.0248		.025			
n			6.5707		6.570			

TABLE VII

H₂-O₃ STOIC

P= 300 PSIA
Q_F= -56.384 KCALS

T°K	2500	3000	3500	3600	3640	3700	4000
a H ₂	.103	.396	.978	1.122		1.269	1.693
b H ₂ O	6.117	5.690	4.705	4.432		4.134	3.122
e O ₂	.038	.132	.296	.335		.371	.466
h OH	.055	.271	.785	.918		1.062	1.500
i H	.005	.057	.349	.474		.632	1.370
j O	.002	.025	.168	.230		.312	.696
n	6.320	6.571	7.281	7.511		7.780	8.847
$\sum n_i \Delta H_i$	148.635	190.876	236.491	246.179		256.106	287.599
Q _{AV}				262.703		230.949	
ΔH	157.254	230.417	361.804	398.788		440.468	595.988
Δh	1.397	2.046	3.213	3.542	3.790	3.912	5.293
$\sum n_i S_i^\circ$	413.054	435.966	471.300	480.766		491.547	531.002
nR ln P	37.850	39.353	43.605	44.983		46.594	52.984
$\sum n_i R \ln \frac{n_i}{n}$	2.240	7.382	16.698	18.815		21.351	28.984
S	377.444	403.995	444.393	454.598		466.304	506.636
s	3.352	3.588	3.947	4.037	4.107	4.141	4.499

TABLE VIII

ENTHALPY - ENTROPY SUMMARY

P = pressure in psia
 Δh = kcal per gram
 s = cal per gram per $^{\circ}\text{K}$

RFNA - NH_3 OVER-OXIDIZED (r = 3.00)

Temp $^{\circ}\text{K}$		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3000	Δh	1.381	1.422			
	s	2.811	2.886			
2500	Δh	1.004	1.012			
	s	2.674	2.739			
2400	Δh	0.943	0.948			
	s	2.649	2.713			
2300	Δh	0.885	0.888			
	s	2.624	2.688			
2000	Δh	0.723	0.724	0.730		
	s	2.549	2.611	2.884		
1500	Δh			0.479	0.479	0.479
	s			2.740	2.802	3.152
1300	Δh			0.390	0.390	
	s			2.677	2.739	
1000	Δh			0.261	0.261	0.261
	s			2.564	2.626	2.976
500	Δh				0.070	0.070
	s				2.362	2.712
400	Δh					0.035
	s					2.634
300	Δh				0.0	0.0
	s				2.185	2.535

RFNA - NH₃ STOICHIOMETRIC (r = 2.21)

Temp °K	P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3000	Δh 1.517 s 2.946	1.57 3.033			
2700	Δh 1.233 s 2.846				
2600	Δh 1.154 s 2.817	1.171 2.889			
2500	Δh 1.080 s 2.788	1.092 2.858			
2000	Δh 0.770 s 2.650	0.772 2.716	0.783 3.005		
1200	Δh s		0.610 2.911		
1500	Δh s		0.510 2.849	0.510 2.914	0.510 3.282
1400	Δh s		0.462 2.815		
1300	Δh s			0.414 2.845	
1000	Δh s		0.278 2.661	0.278 2.726	0.277 3.094
500	Δh s				0.074 2.813
300	Δh s				0.0 2.626

RFNA - NH₃ UNDER-OXIDIZED (r = 1.50)

Temp ^o K	P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3000	Δ h s 1.548 3.272	1.583 3.362			
2500	Δ h s 1.169 3.134	1.172 3.213			
2100	Δ h s 0.920 3.026	0.921 3.103			
2000	Δ h s 0.861 2.997	0.861 3.074	0.864 3.413		
1500	Δ h s		0.577 3.248	0.577 3.326	0.577 3.764
1400	Δ h s		0.418 3.130		
1000	Δ h s		0.317 3.038	0.317 3.116	0.317 3.553
900	Δ h s		0.268 2.987	0.268 3.064	
800	Δ h s			0.221 3.008	
500	Δ h s			0.086 2.797	0.086 3.234
400	Δ h s				0.042 3.138
300	Δ h s				0.0 3.017

$\text{NH}_3 - \text{O}_3$ OVER-OXIDIZED ($r = 2.00$)

Temp ^o K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3500	Δh s	2.041 3.044	2.208 3.160			
3400	Δh s	1.888 2.999				
3300	Δh s	1.749 2.958	1.850 3.055			
3200	Δh s		1.704 3.009			
3000	Δh s	1.415 2.852	1.458 2.930	1.940 3.379		
2500	Δh s		1.034 2.776	1.107 3.080		
2000	Δh s			0.747 2.920	0.747 2.984	
1500	Δh s			0.488 2.773	0.488 2.835	0.488 3.187
1000	Δh s					0.266 3.008
500	Δh s					0.071 2.739

NH₃ - O₃ STOICHIOMETRIC (r = 1.41)

Temp ^o K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3500	Δh s	2.351 3.278	2.554 3.412			
3400	Δh s	2.167 3.225				
3300	Δh s	2.001 3.175	2.132 3.288			
3200	Δh s		1.956 3.233			
3000	Δh s	1.597 3.046	1.658 3.137	2.267 3.657		
2500	Δh s		1.146 2.951	1.260 3.294	1.311 3.383	
2000	Δh s			0.819 3.099	0.824 3.169	
1800	Δh s			0.691 3.031	0.691 3.098	
1500	Δh s			0.533 2.934	0.533 3.001	0.533 3.380
1000	Δh s					0.289 3.183

$\text{NH}_3 - \text{O}_3$ UNDER-OXIDIZED ($r = 1.10$)

Temp°K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3500	Δh s	2.275 3.508	2.469 3.647			
3200	Δh s	1.810 3.369	1.892 3.474			
3100	Δh s	1.692 3.332	1.750 3.429			
3000	Δh s	1.588 3.297	1.628 3.389	2.164 3.919		
2500	Δh s		1.195 3.232	1.249 3.590		
2000	Δh s			0.878 3.426	0.879 3.504	
1700	Δh s			0.699 3.329	0.699 3.406	
1500	Δh s			0.585 3.258	0.585 3.335	0.585 3.770
1000	Δh s					0.320 3.556
500	Δh s					0.086 3.233

NH₃ - O₃ UNDER-OXIDIZED (r = 0.80)

Temp ^o K	P = 600	P = 300	P = 14.7	P = 7.35	P = .147
3500	Δh s	2.563 3.994			
3000	Δh s	1.754 3.660	1.771 3.752		
2600	Δh s	1.391 3.526	1.398 3.619		
2500	Δh s	1.317 3.497	1.321 3.589	1.377 4.004	
2000	Δh s		0.975 3.826		
1500	Δh s		0.653 3.641	0.653 3.731	0.653 4.238
1400	Δh s		0.592 3.599		
1300	Δh s		0.532 3.555	0.533 3.648	
1200	Δh s		0.474 3.508	0.474 3.599	
1100	Δh s			0.417 3.548	
1000	Δh s		0.360 3.404	0.360 3.494	0.360 4.002
500	Δh s				0.098 3.640

$H_2 - O_3$ OVER-OXIDIZED ($r = 9.92$)

Temp ^o K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
4000	Δh	3.935	4.555			
	s	3.839	4.087			
3800	Δh	3.274				
	s	3.670				
3700	Δh	2.993	3.350			
	s	3.595	3.774			
3600	Δh		3.028			
	s		3.686			
3500	Δh	2.516	2.746	5.345		
	s	3.462	3.607	4.745		
3000	Δh	1.706	1.765	2.431	2.777	
	s	3.213	3.306	3.858	4.055	
2500	Δh			1.334	1.383	2.367
	s			3.464	3.555	4.380
2000	Δh			0.885	0.889	0.943
	s			3.266	3.338	3.764

H₂ - O₃ STOICHIOMETRIC (r = 7.94)

Temp°K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
4000	Δh s	4.580 4.217	5.293 4.499			
3800	Δh s	3.819 4.023				
3700	Δh s	3.495 3.936	3.912 4.141			
3600	Δh s		3.542 4.037			
3500	Δh s	2.936 3.780	3.213 3.947	6.204 5.246		
3000	Δh s	1.965 3.481	2.046 3.588	2.869 4.229	3.278 4.457	
2500	Δh s		1.397 3.352	1.549 3.752	1.617 3.859	2.825 4.821
2000	Δh s			0.992 3.507	0.999 3.587	1.092 4.069
1800	Δh s					0.833 3.930

$H_2 - O_3$ UNDER-OXIDIZED ($r = 6.61$)

Temp ^o K		P = 600	P = 300	P = 14.7	P = 7.35	P = .147
4000	Δh	4.680	5.454			
	s	4.600	4.910			
3800	Δh	3.861				
	s	4.391				
3700	Δh	3.516	3.957			
	s	4.298	4.522			
3600	Δh		3.561			
	s		4.411			
3500	Δh	2.933	3.213	6.460		
	s	4.136	4.314	5.738		
3000	Δh	2.000	2.058	2.836	3.267	
	s	3.850	3.960	4.632	4.880	
2500	Δh		1.490	1.565	1.611	2.778
	s		3.754	4.177	4.286	5.294
2000	Δh			1.086	1.090	1.124
	s			3.966	4.057	4.582
1500	Δh					0.719
	s					4.350
1000	Δh					0.391
	s					4.084

H₂ - O₃ UNDER-OXIDIZED (r = 4.96)

Temp°K		P=600	P = 300	P = 14.7	P = 7.35	P = .147
4000	Δh s	5.108 5.367	5.949 5.717			
3600	Δh s	3.569 4.960				
3500	Δh s	3.299 4.886	3.560 5.083	7.072 6.690		
3400	Δh s		3.256 4.994			
3000	Δh s	2.359 4.598	2.411 4.732	3.125 5.490	3.556 5.760	
2500	Δh s		1.781 4.503	1.863 5.037	1.908 5.171	3.023 6.297
2000	Δh s			1.307 4.791	1.308 4.907	1.357 5.579
1500	Δh s					0.870 5.301
1000	Δh s					0.477 4.983
800	Δh s					0.332 4.822

TABLE IX

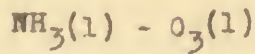
PERFORMANCE SUMMARY

RFNA - NH₃(1)

r	P _c	P _e	C	I _{sp}	T _c °K	T _e °K
3.00	300	14.7	6645	207	2325	1360
2.21 (stoic.)	300	14.7	7323	228	2599	1630
1.50	300	14.7	6898	214	2062	1110
3.00	600	14.7	7161	223	2331	1170
2.21 (stoic.)	600	14.7	7942	247	2621	1425
1.50	600	14.7	7384	230	2063	955
3.00	300	7.35	7167	223	2325	1190
2.21 (stoic.)	300	7.35	7914	246	2599	1425
1.50	300	7.35	7384	230	2062	955
3.00	600	7.35	7576	236	2331	1010
2.21 (stoic.)	600	7.35	8437	262	2621	1240
1.50	600	7.35	7782	242	2063	810
3.00	300	.147	8721	271	2325	480
2.21 (stoic.)	300	.147	9751	303	2599	615
1.50	300	.147	8869	276	2062	350
3.00	600	.147	8854	275	2331	400
2.21 (stoic.)	600	.147	9920	308	2621	515
1.50	600	.147	8996	280	2063	300

TABLE IX

PERFORMANCE SUMMARY



r	P _c	P _e	C	I _{sp}	T _c °K	T _e °K
2.00	300	14.7	8486	264	3280	2400
1.41 (stoic.)	300	14.7	8930	278	3285	2460
1.10	300	14.7	8901	277	3124	2050
0.80	300	14.7	8292	258	2564	1423
2.00	600	14.7	9233	287	3352	2200
1.41 (stoic.)	600	14.7	9749	303	3362	2290
1.10	600	14.7	9649	300	3179	1802
0.80	600	14.7	8910	277	2573	1220
2.00	300	7.35	9199	286	3280	2200
1.41 (stoic.)	300	7.35	9692	301	3285	2280
1.10	300	7.35	9621	299	2124	1805
0.80	300	7.35	8921	277	2564	1230
2.00	600	7.35	9873	307	3352	2185
1.41 (stoic.)	600	7.35	10414	324	3362	2100
1.10	600	7.35	10233	318	3179	1580
0.80	600	7.35	9412	293	2573	1050
2.00	300	.147	11684	363	3280	1100
1.41 (stoic.)	300	.147	12409	386	3285	1220
1.10	300	.147	11872	369	3124	796
0.80	300	.147	10786	335	2564	465
2.00	600	.147	11936	371	3352	1140
1.41 (stoic.)	600	.147	12721	396	3362	1060
1.10	600	.147	12132	377	3179	665
0.80	600	.147	10972	341	2573	380

TABLE IX

PERFORMANCE SUMMARY



r	Pc	Pe	c	I _{SD}	T _c ^o K	T _c ^o K
9.92	300	14.7	10129	315	3634	2870
7.94 (stoic.)	300	14.7	10613	330	3640	2900
6.61	300	14.7	11107	345	3607	2820
4.96	300	14.7	11762	366	3447	2500
9.92	600	14.7	11059	344	3752	2770
7.94 (stoic.)	600	14.7	11665	363	3760	2815
6.61	600	14.7	12227	380	3721	2710
4.96	600	14.7	12816	398	3537	2280
9.92	300	7.35	11021	343	3634	2735
7.94 (stoic.)	300	7.35	11629	362	3640	2765
6.61	300	7.35	12113	377	3607	2670
4.96	300	7.35	12768	397	3447	2275
9.92	600	7.35	11856	368	3752	2625
7.94 (stoic.)	600	7.34	12521	389	3760	2675
6.61	600	7.35	13081	407	3721	2550
4.96	600	7.35	13651	424	3537	2010
9.92	300	.147	14391	447	3634	1920
7.94 (stoic.)	300	.147	15217	473	3640	2015
6.61	300	.147	15768	490	3607	1650
4.96	300	.147	16081	500	3447	1080
9.92	600	.147	14819	461	3752	1710
7.94 (stoic.)	600	.147	15739	489	3760	1910
6.61	600	.147	16214	504	3721	1430
4.96	600	.147	16442	511	3537	910

TABLE X

FROZEN PERFORMANCE SUMMARY

RFNA - NH₃

r	P _c	P _e	c	I _{sp}	T _c °K	T _e °K
3.00	300	14.7	6563	204	2325	1315
2.21 (stoic.)	300	14.7	7199	224	2599	1505
1.50	300	14.7	6898	214	2062	1110

NH₃ - O₃

2.00	300	14.7	8155	254	3200	1882
1.41 (stoic.)	300	14.7	8544	266	3285	1900
1.10	300	14.7	8643	269	3124	1780
0.80	300	14.7	8232	256	2564	1395

H₂ - O₃

9.92	300	14.7	9578	298	3634	2095
7.94 (stoic.)	300	14.7	10091	314	3640	2100
6.61	300	14.7	10566	329	3721	2060
4.96	300	14.7	11306	352	3447	1960

APPENDIX I

FROZEN FLOW

It is assumed in the body of this thesis that equilibrium exists throughout the expansion process. This may not be correct since during expansion the gases undergo a very rapid change of temperature and pressure so that equilibrium may not be maintained to exhaust conditions. Therefore it is valuable to calculate performance of rocket propellants assuming "frozen" flow. This assumes that the composition of the gases is the same at exhaust conditions as it is at the chamber conditions. Frozen flow represents the amount of energy obtained from the process due only to the decrease in sensible heat with the drop in temperature. This is the least energy obtainable from the expansion and represents one of two extremes of the expansion process.

In all probability the composition of the combustion gases at the exhaust temperature and pressure lies somewhere between the equilibrium and frozen flow.

For the frozen composition calculations it is assumed that the change in composition of each component is linear within the 100-degree interval bracketing the chamber temperature. Accordingly, the composition at the theoretical chamber temperature is calculated and held constant during expansion.

The procedure used in calculating Δh and s is the same as in the case of equilibrium flow except that the composition at the exhaust conditions is considered to be the same as that in the chamber.

Performances for the three systems considered were calculated for a chamber pressure of 300 psia and an exhaust pressure of 14.7 psia. These values are included in Table T-10. Frozen flow appears as dotted lines on the enthalpy-entropy diagrams.

SOLID LINES. EQUILIBRIUM FLOW

DASHED LINE. CONSTANT COMPOSITION FLOW

SPECIFIC IMPULSE - I_{sp} - SECONDS

320

300

280

260

240

220

200

180

$P_c = 14.7$ PSIA

$P_c = 7.35$ PSIA

$P_c = 14.7$ PSIA

STOIC. MIXTURE RATIO

FIGURE 1

I_{sp} VERSUS r
 NH_3 -RFNA SYSTEM
 $P_c = 300$ PSIA

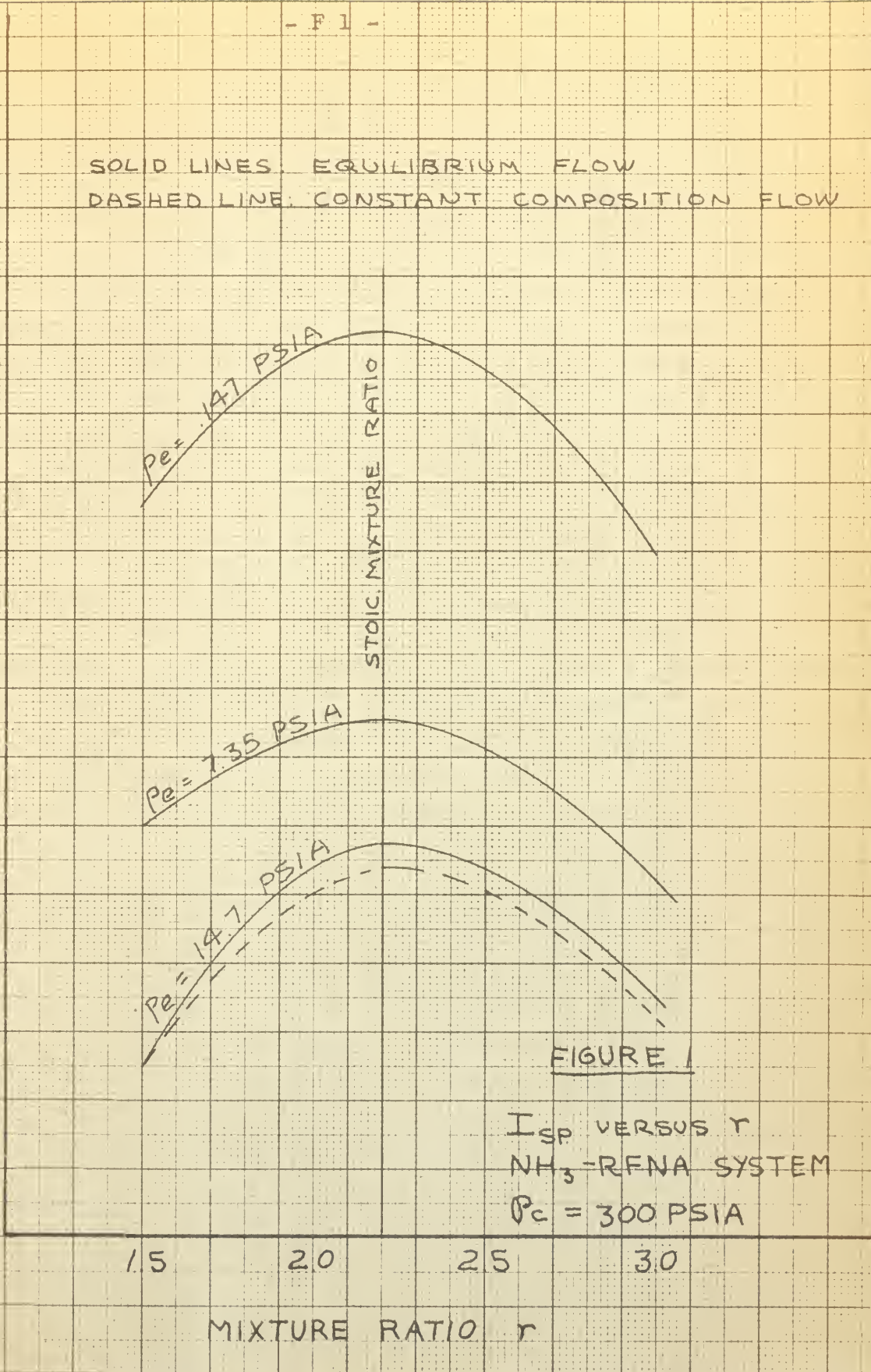
1.5

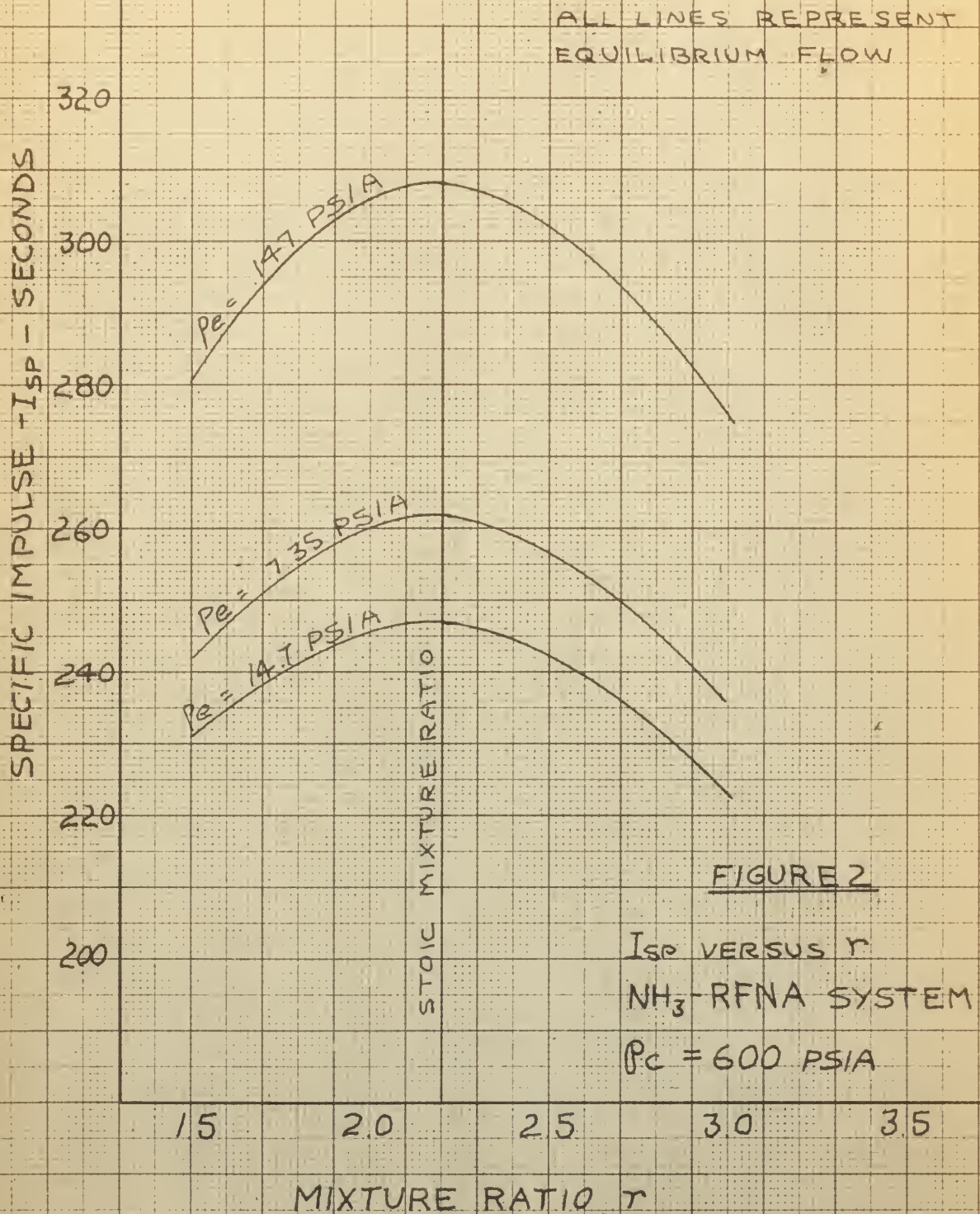
2.0

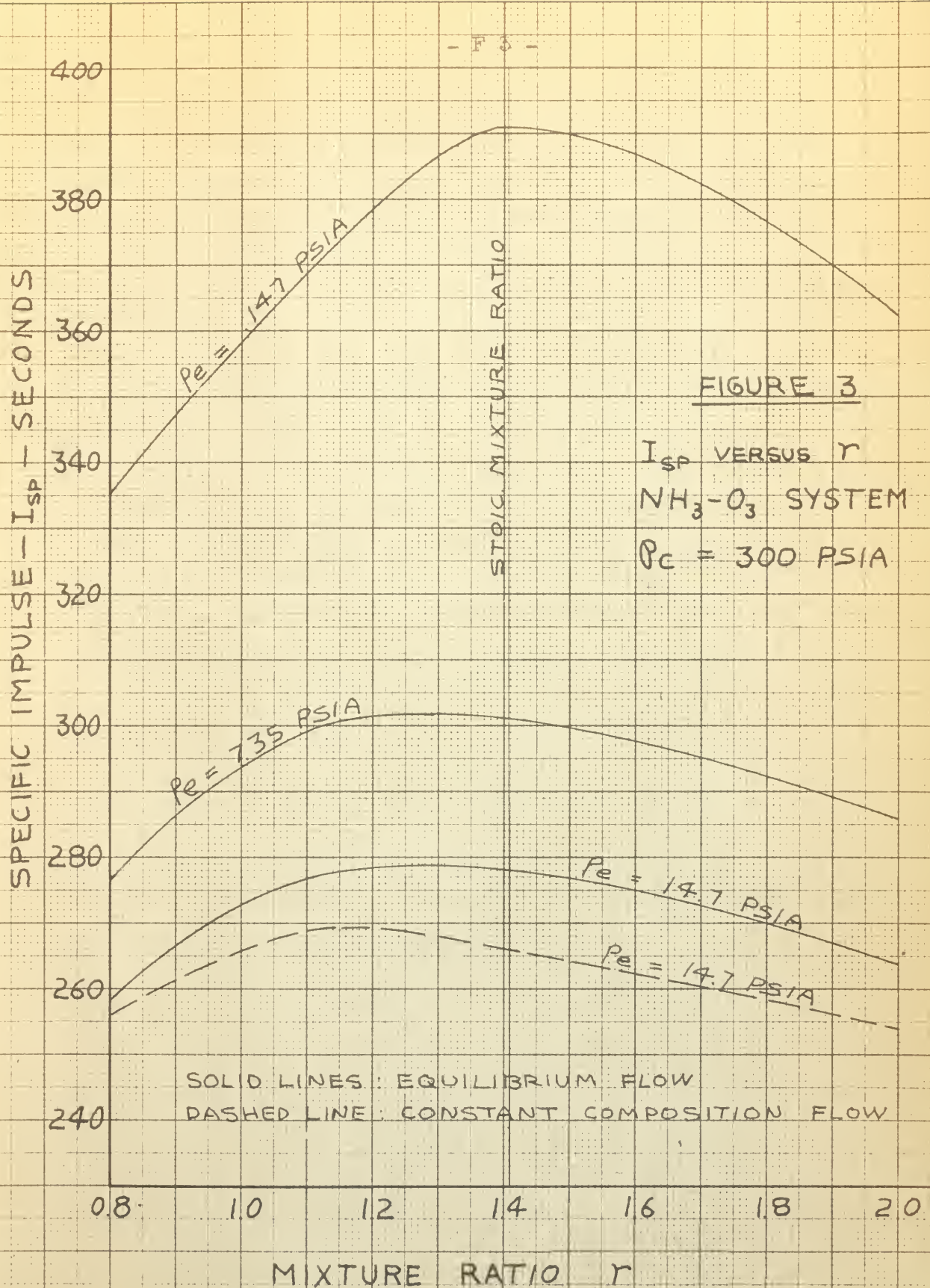
2.5

3.0

MIXTURE RATIO r







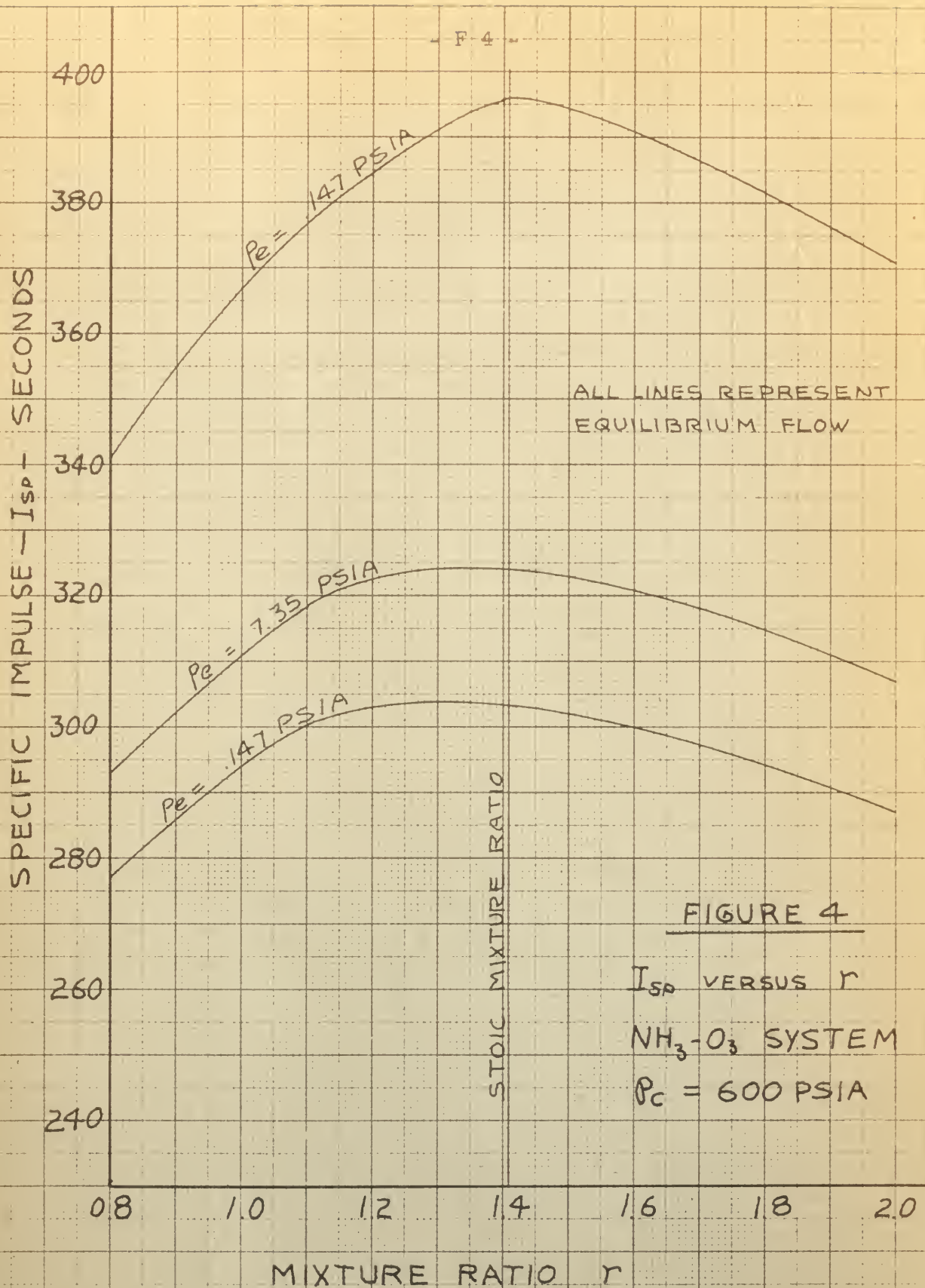
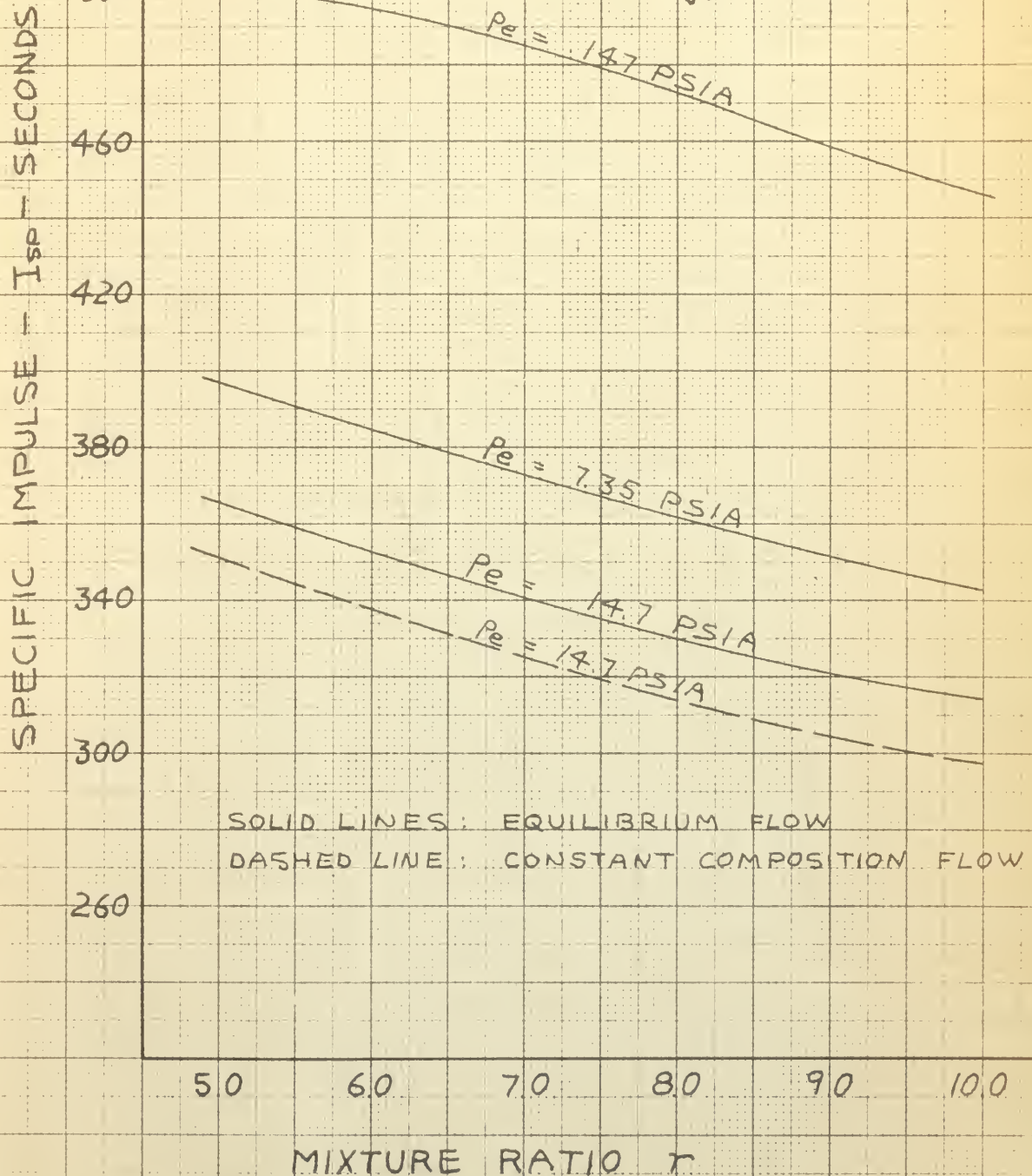


FIGURE 5

I_{sp} VERSUS r

H_2-O_2 SYSTEM

$P_c = 300$ PSIA



SPECIFIC IMPULSE - I_{sp} - SECONDS

500
480
460
440
420
400
380
360
340

ALL LINES REPRESENT EQUILIBRIUM FLOW

FIGURE 6

I_{sp} VERSUS γ
 H_2-O_3 SYSTEM
 $P_c = 600$ PSIA

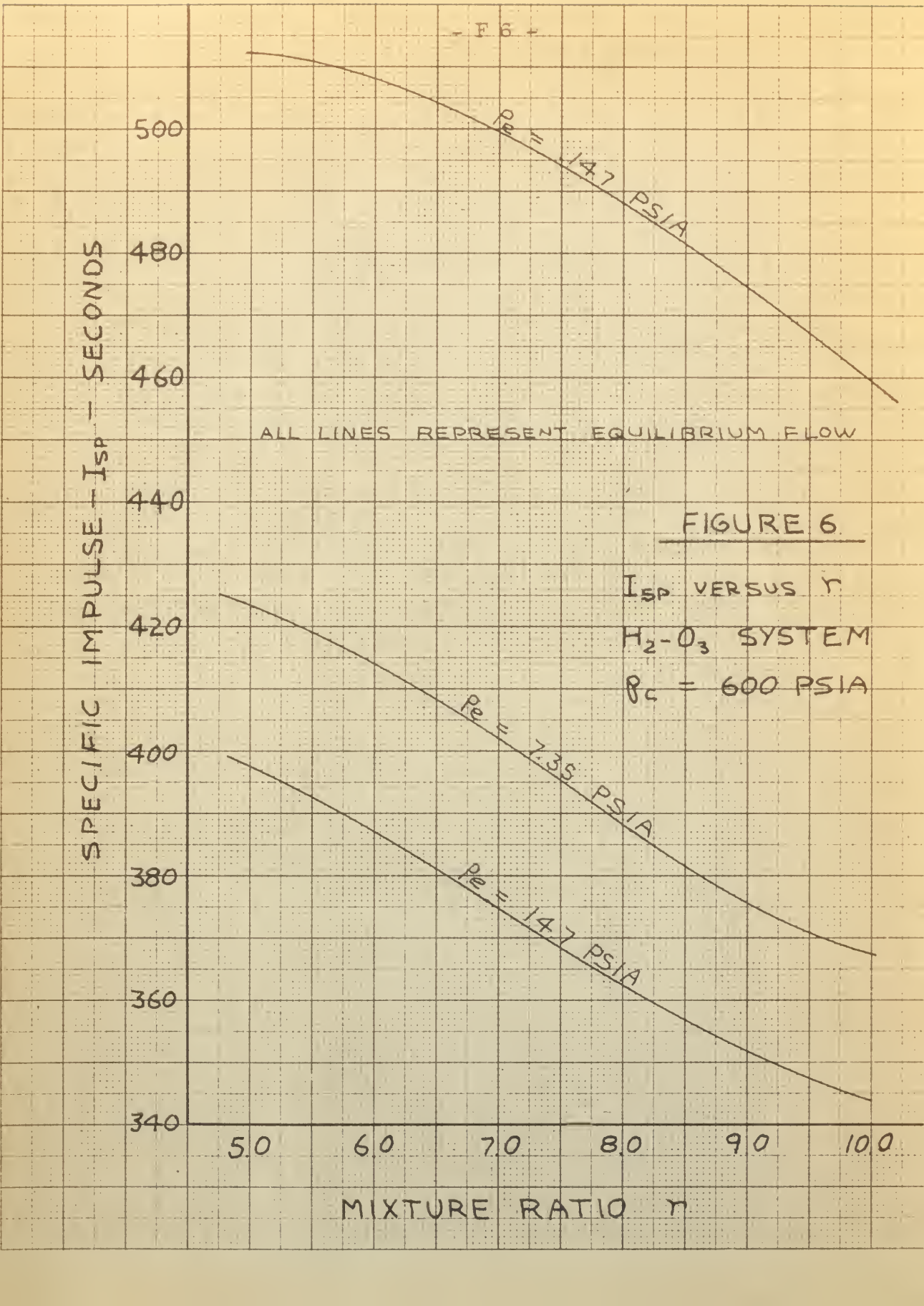
$P_e = 14.7$ PSIA

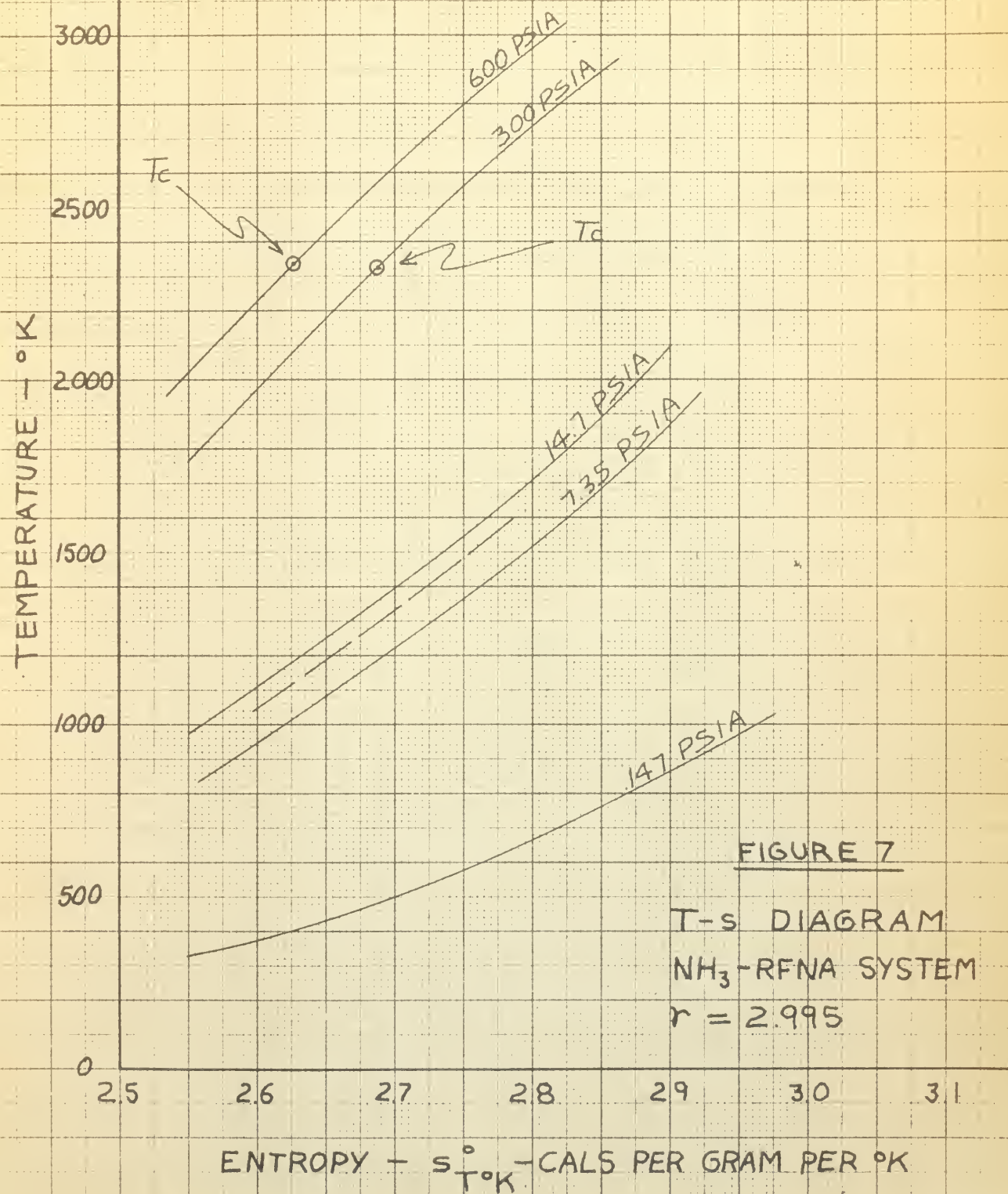
$P_e = 7.35$ PSIA

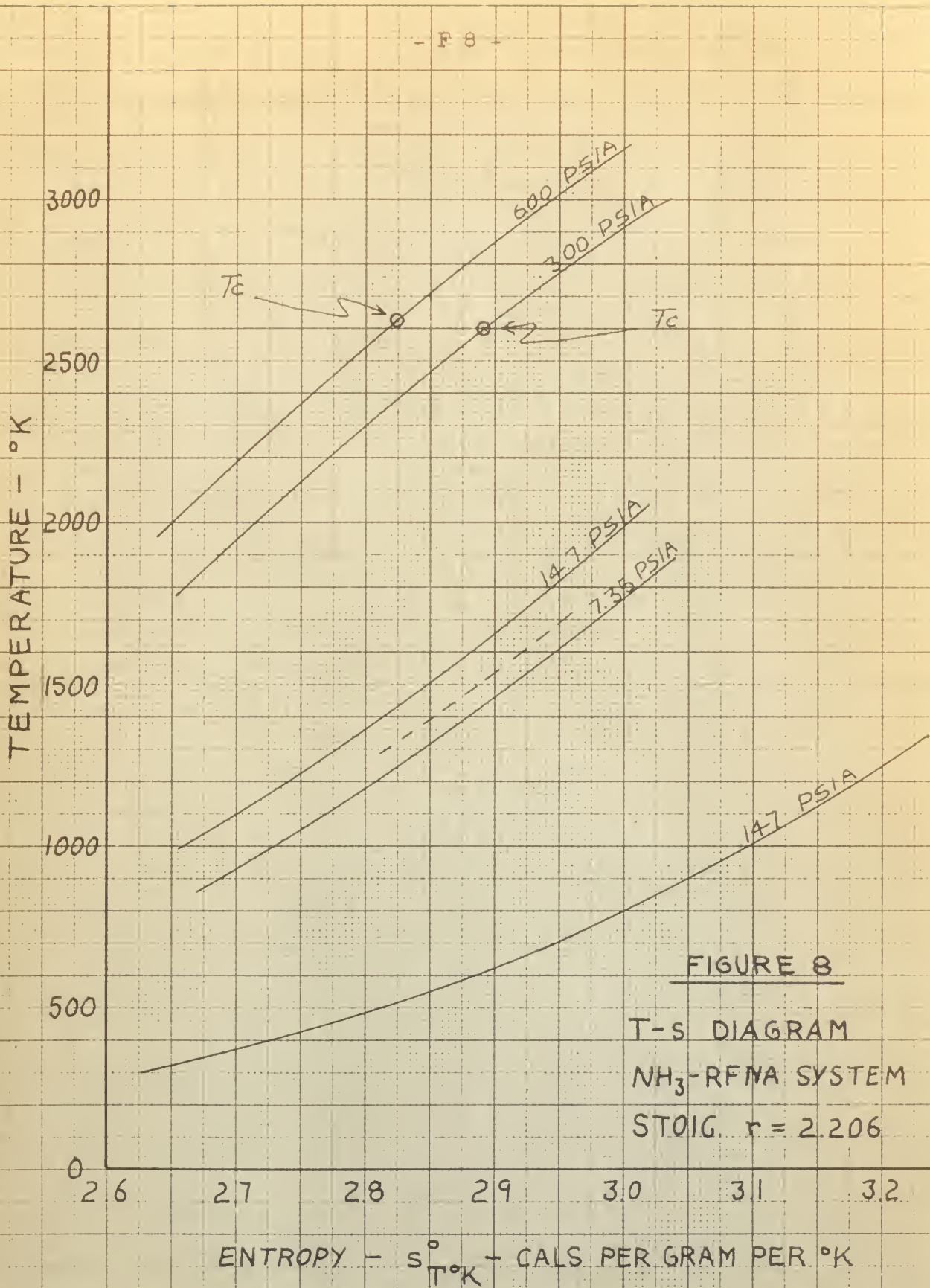
$P_e = 14.7$ PSIA

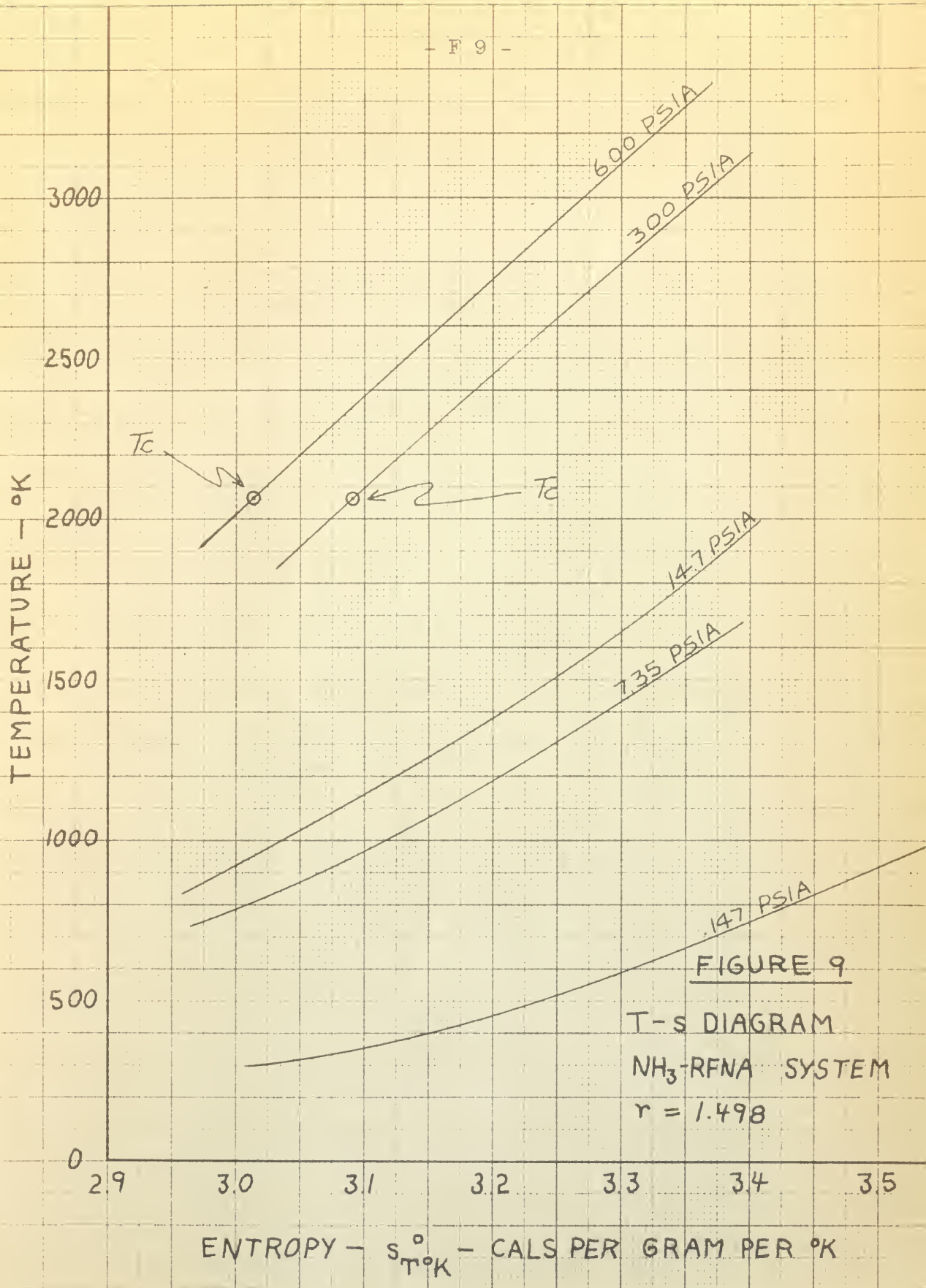
5.0 6.0 7.0 8.0 9.0 10.0

MIXTURE RATIO γ









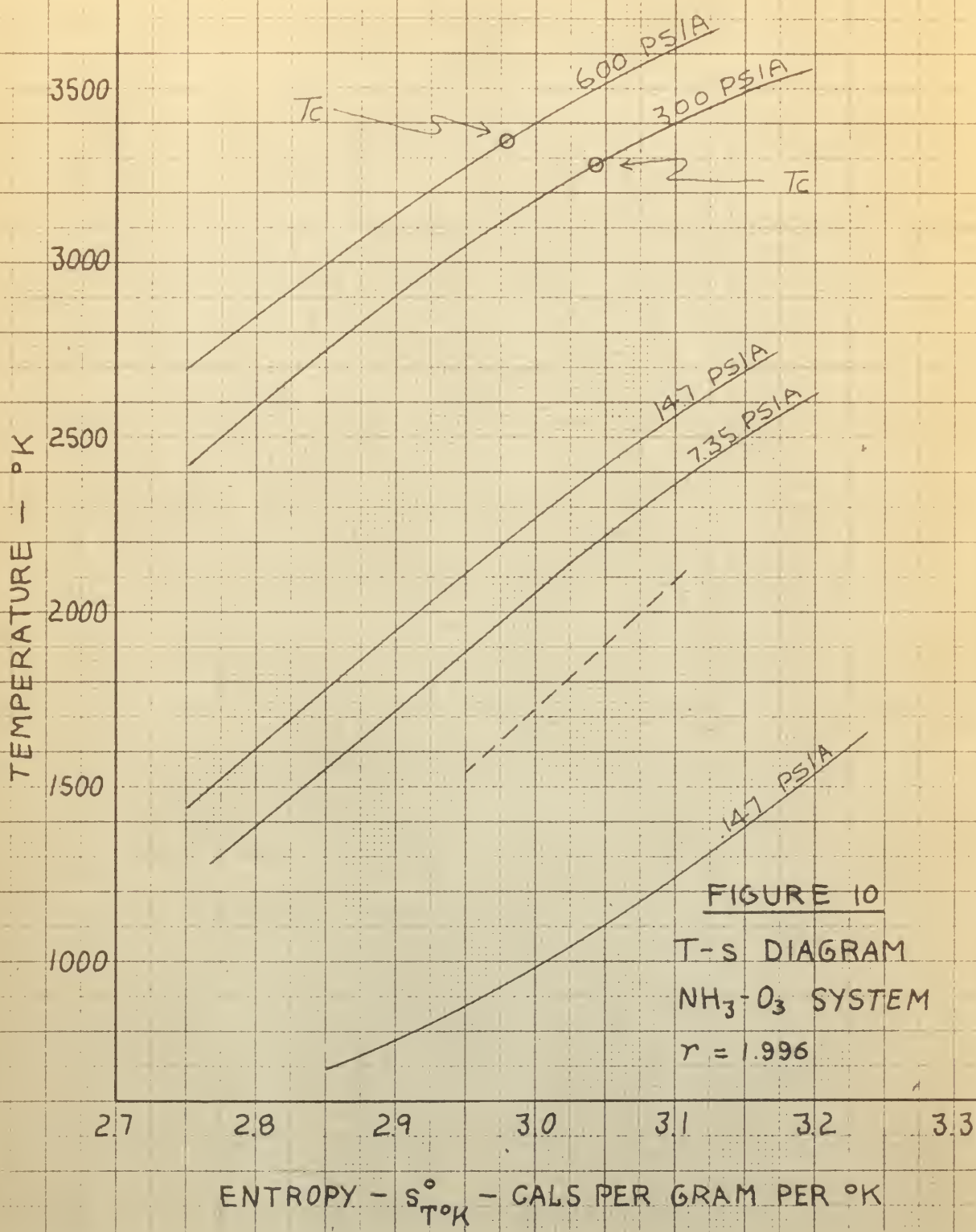
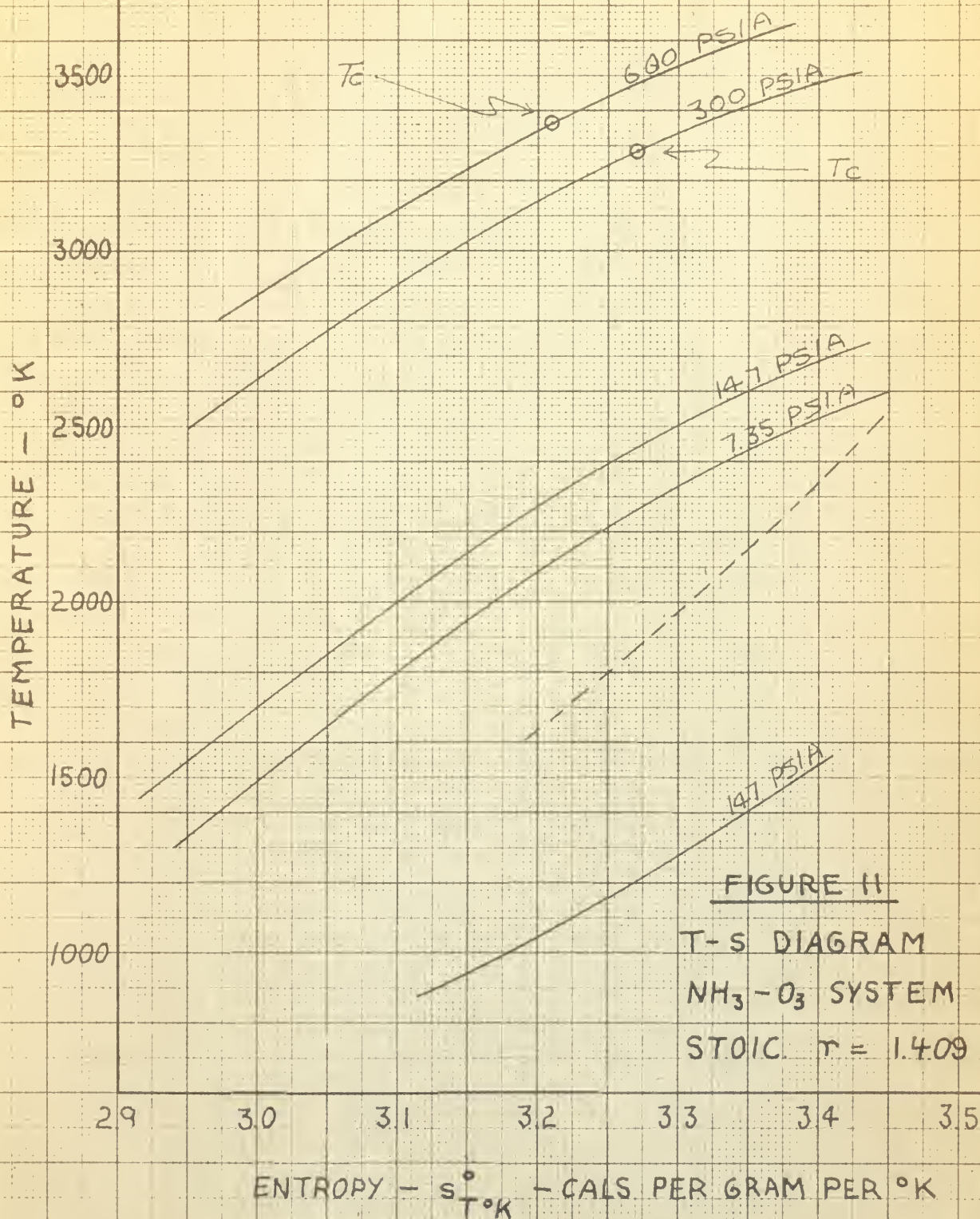


FIGURE 10
T-s DIAGRAM
NH₃-O₃ SYSTEM
 $r = 1.996$



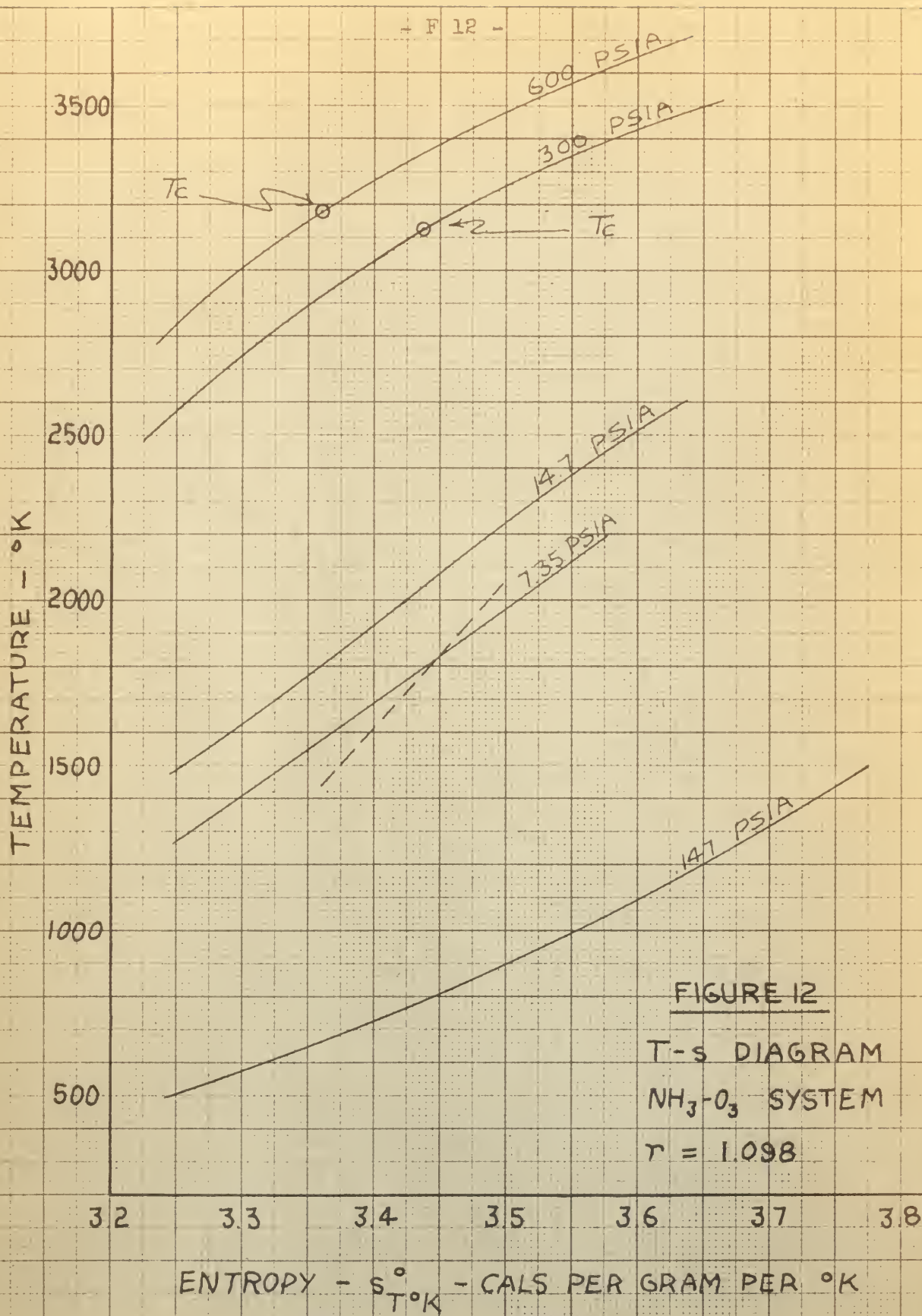
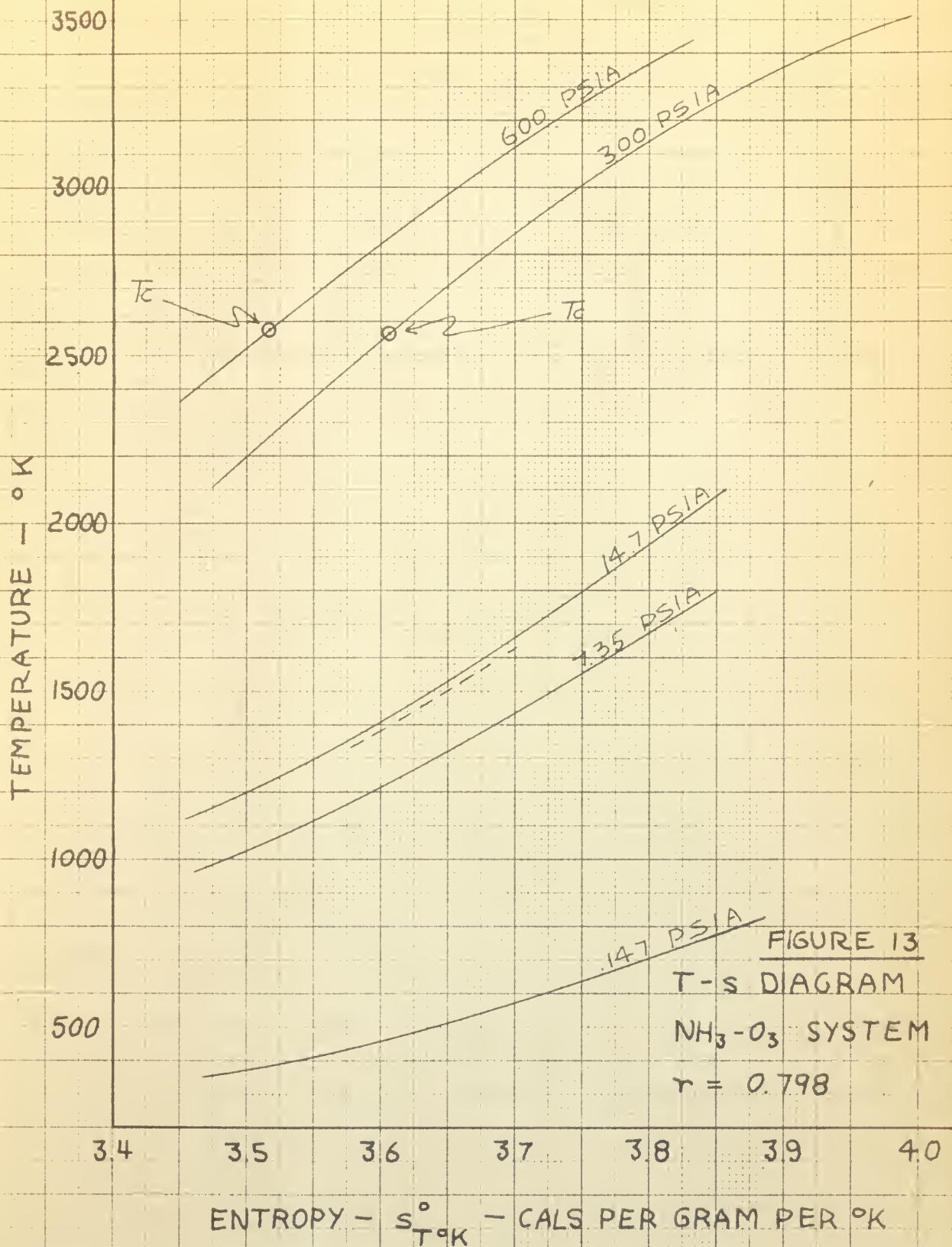


FIGURE 12
T-s DIAGRAM
NH₃-O₃ SYSTEM
 $r = 1.098$



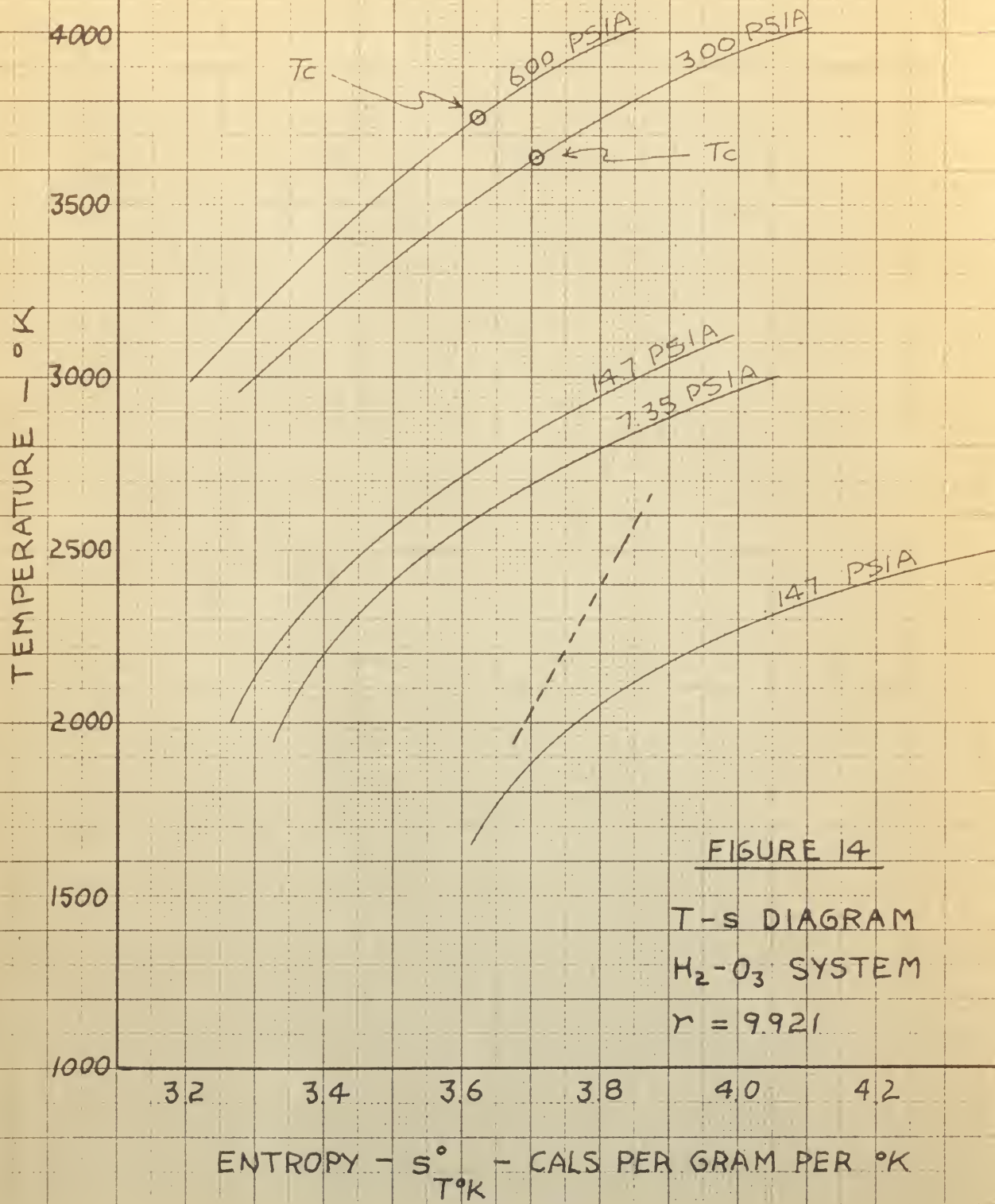
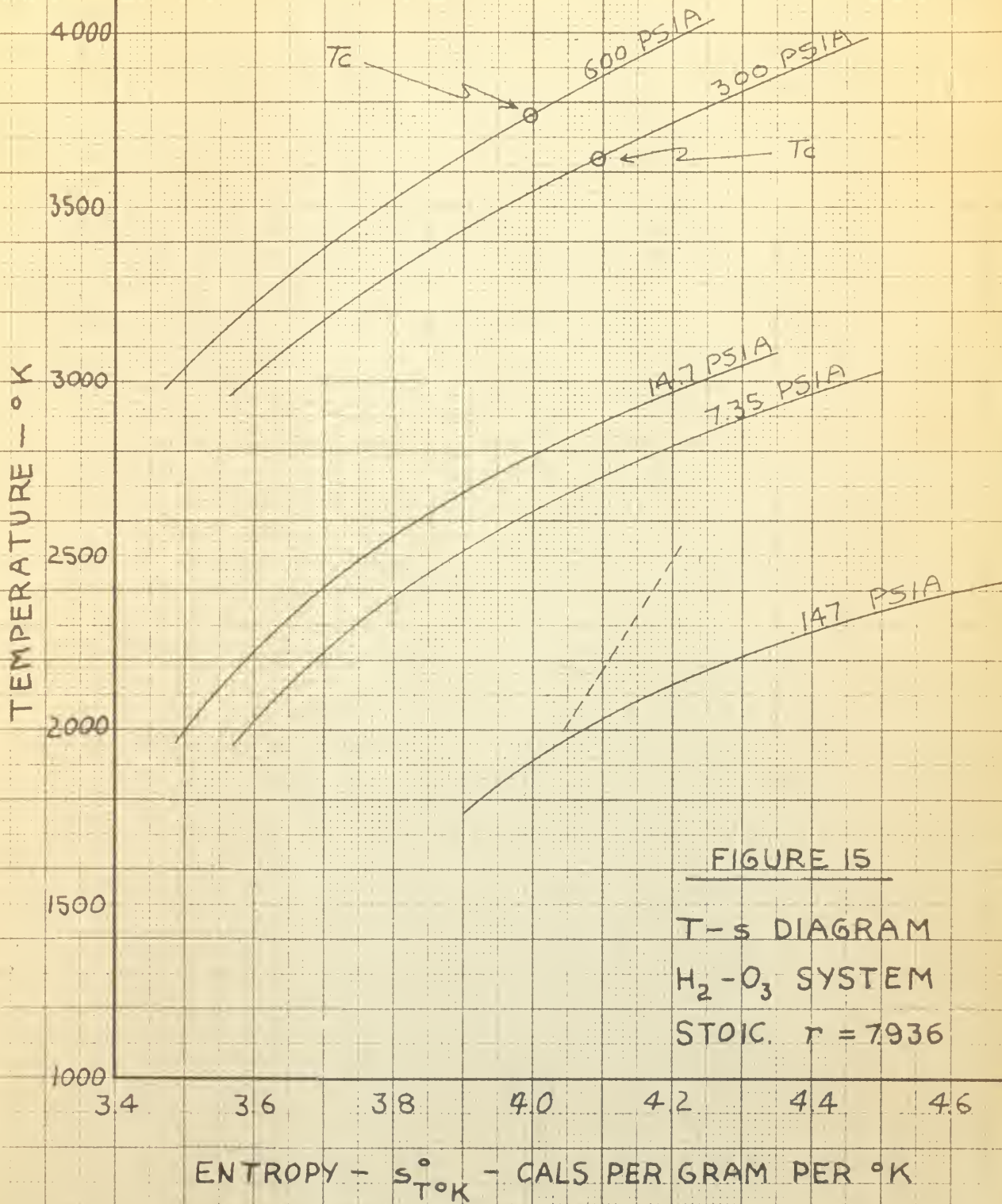
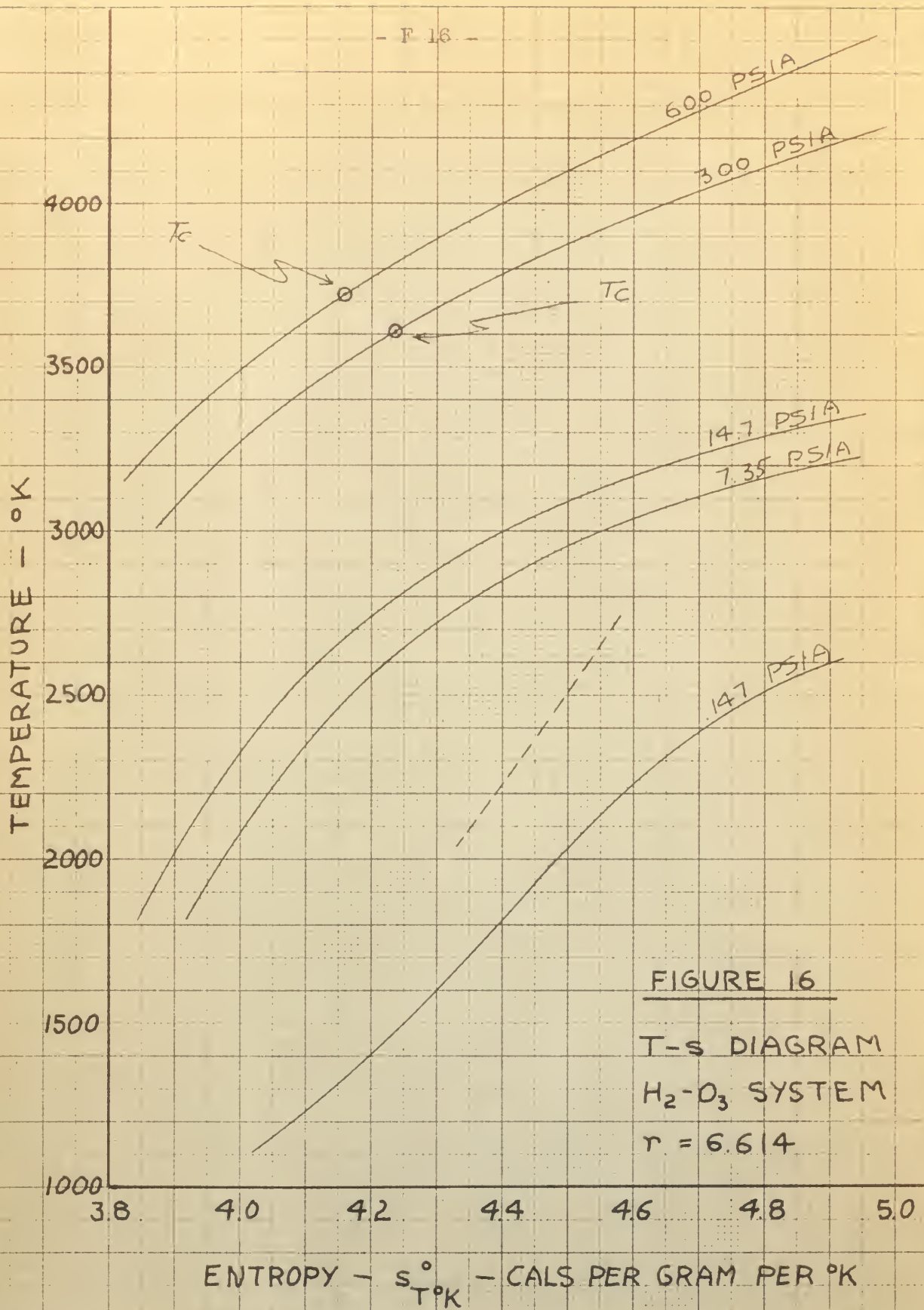


FIGURE 14
T-s DIAGRAM
H₂-O₃ SYSTEM
 $r = 9.921$





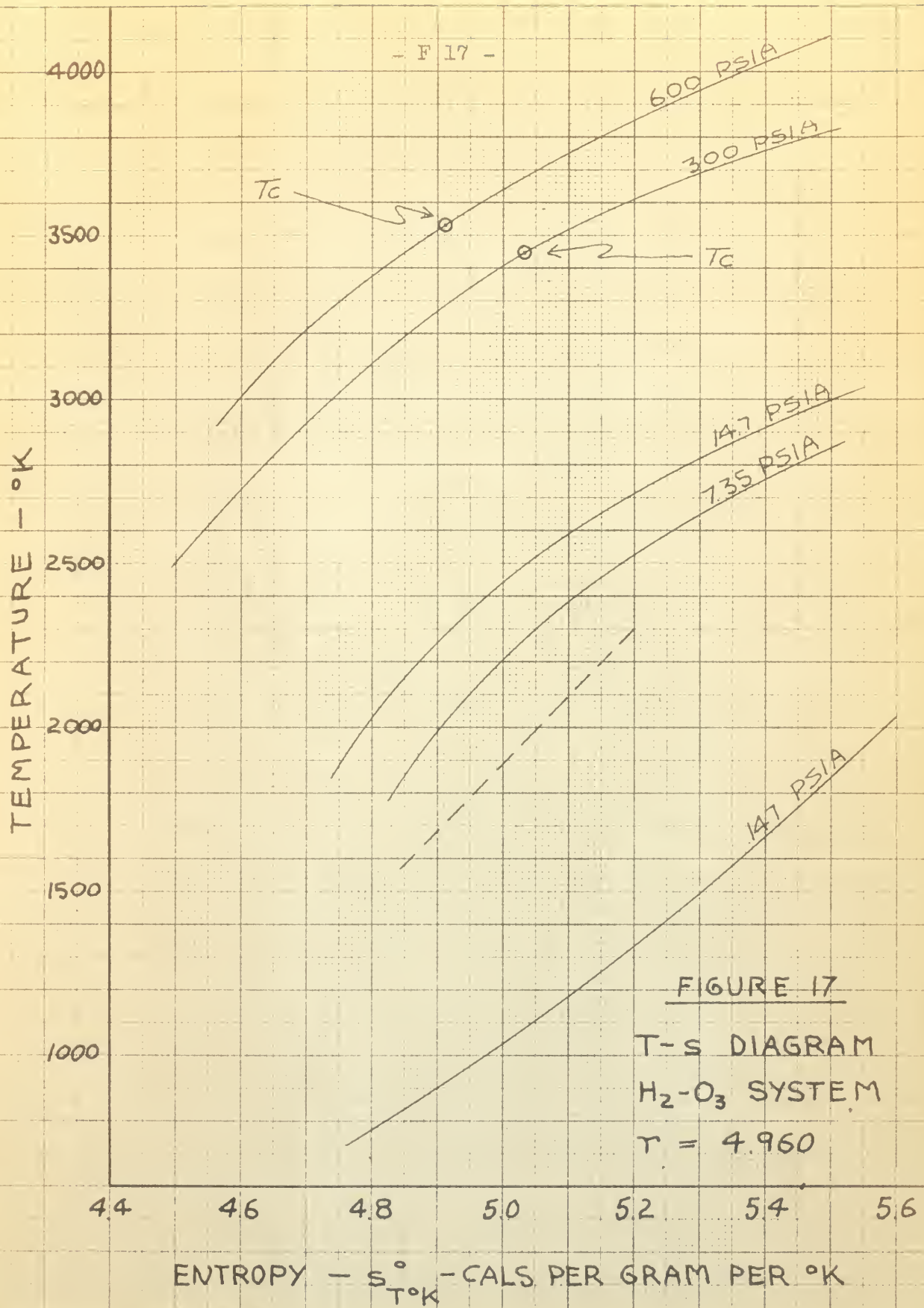
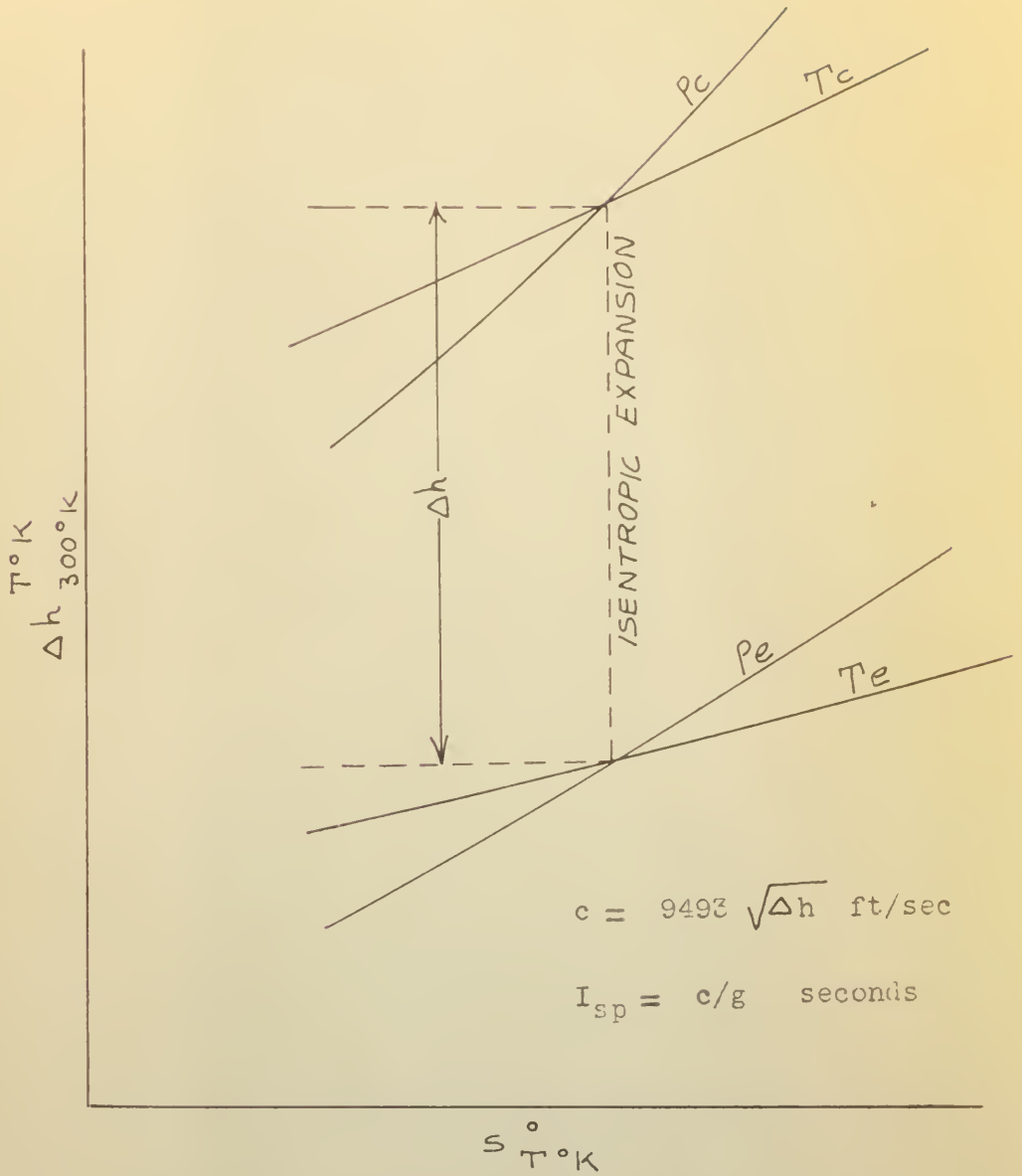
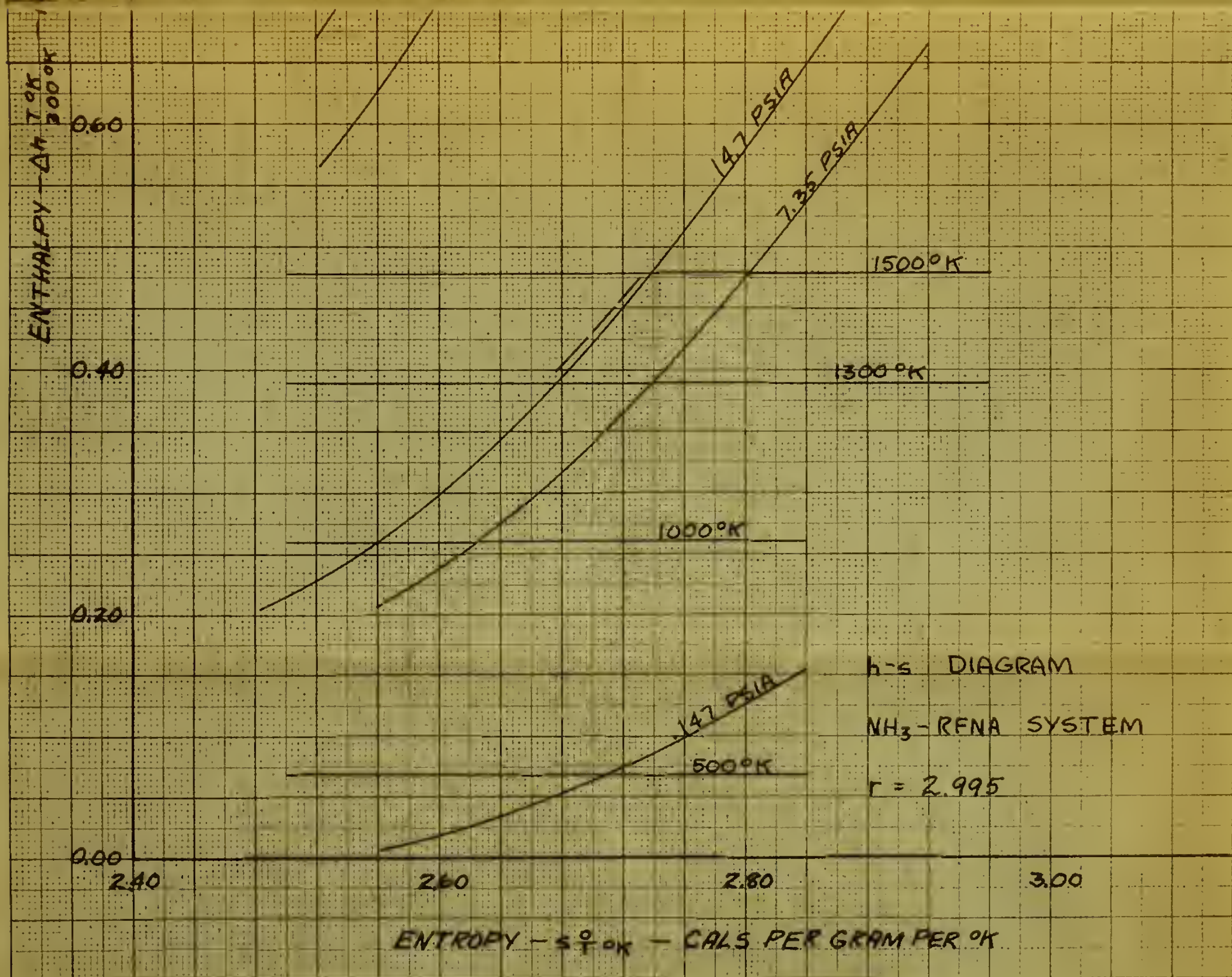
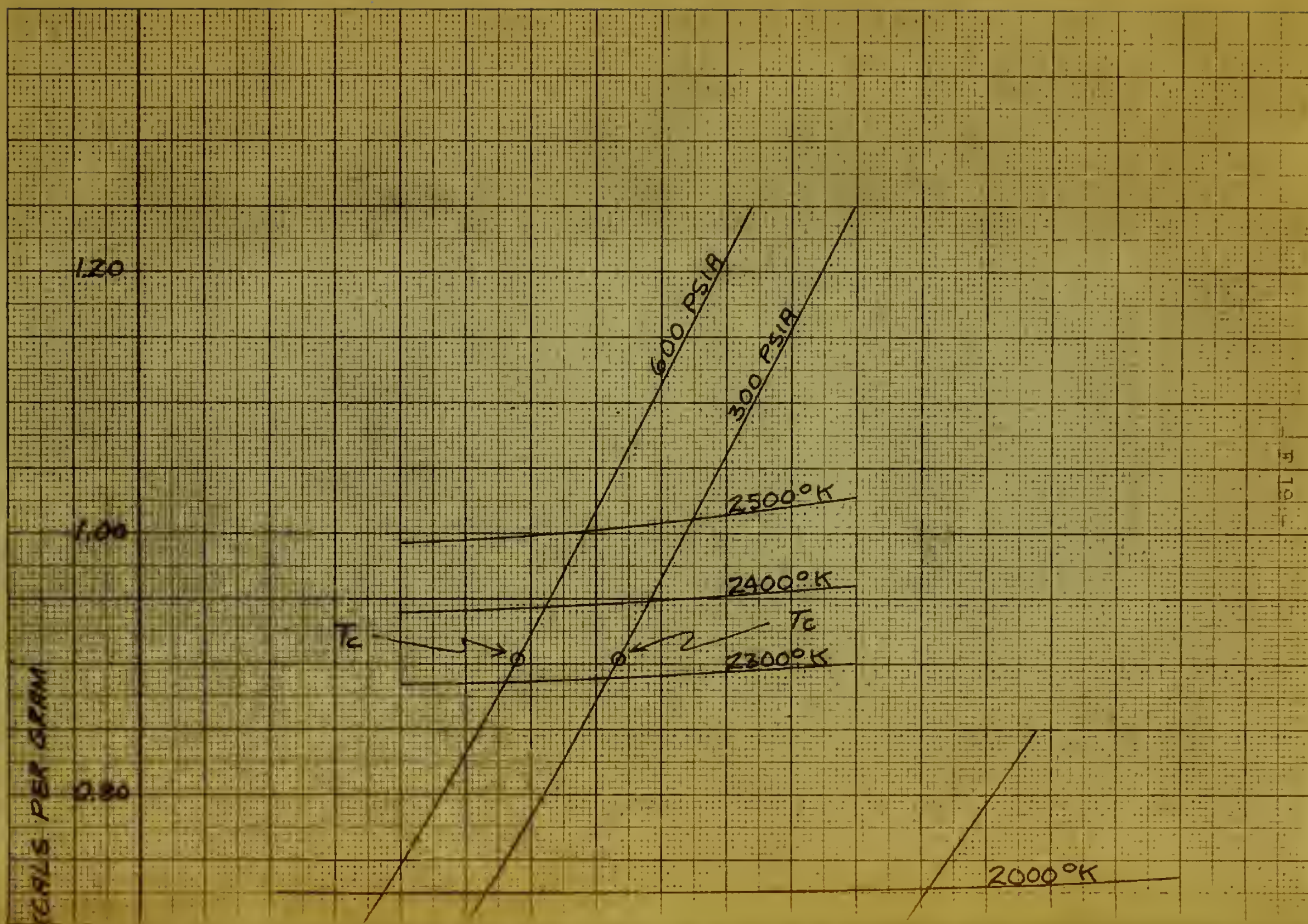
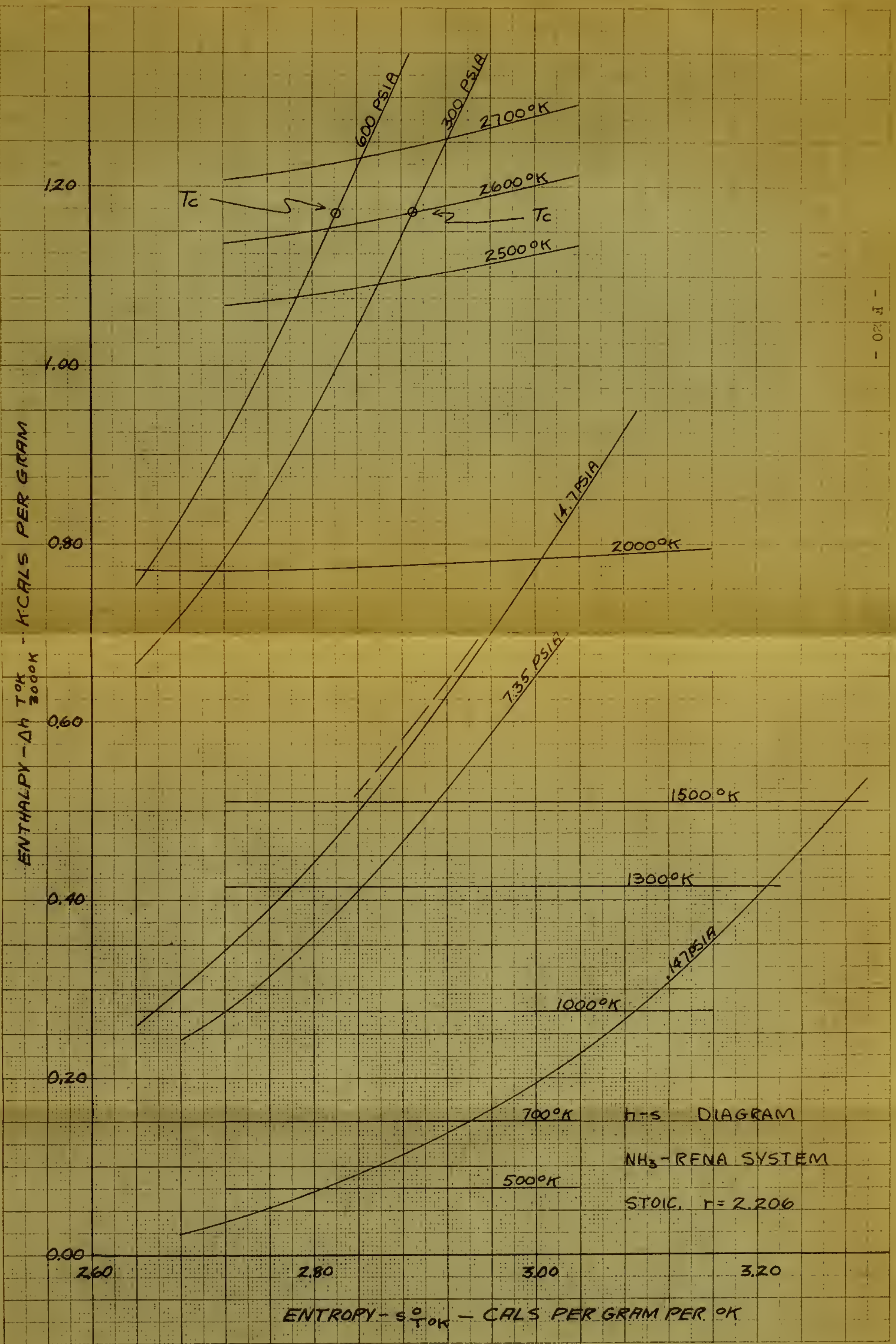


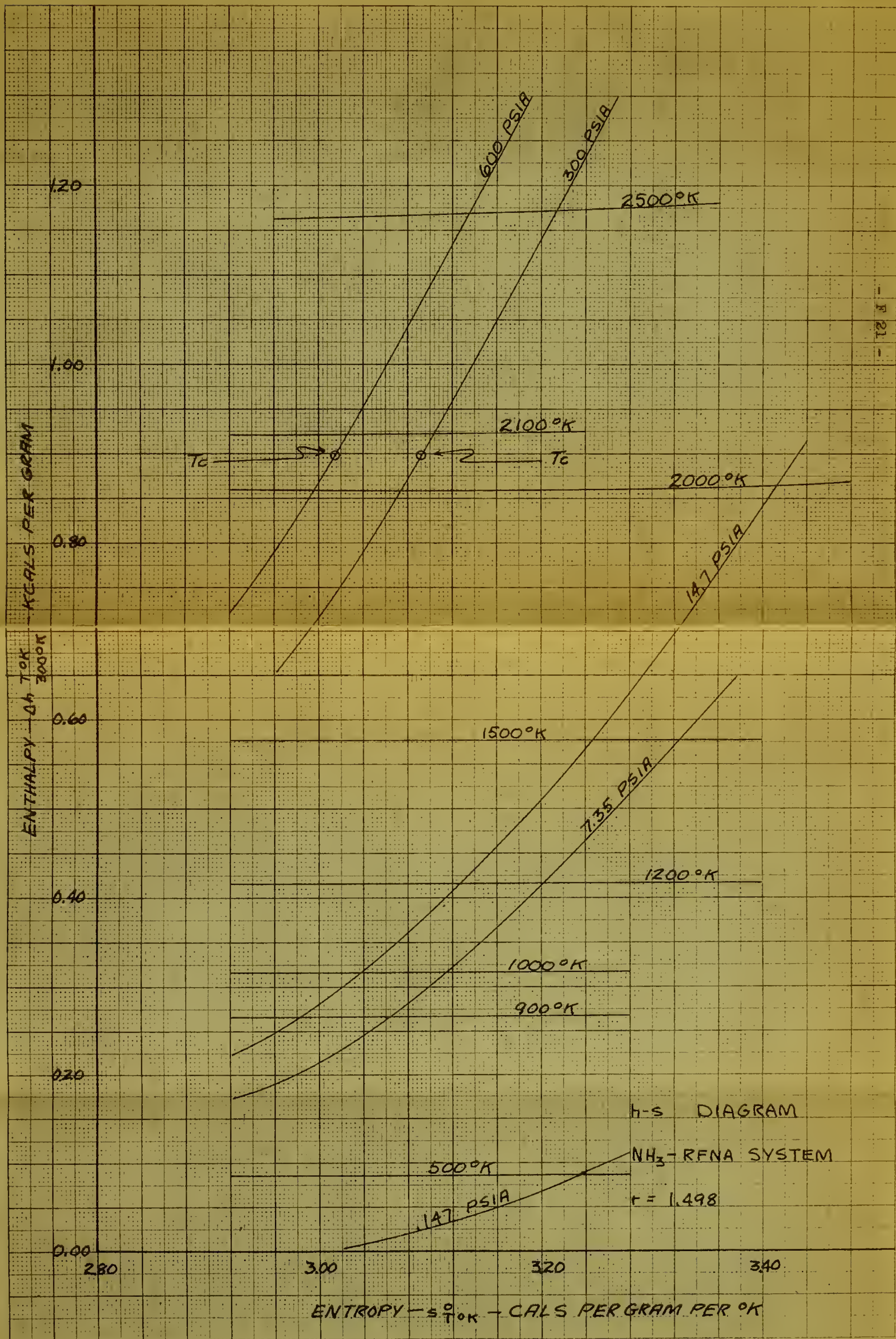
FIGURE 18

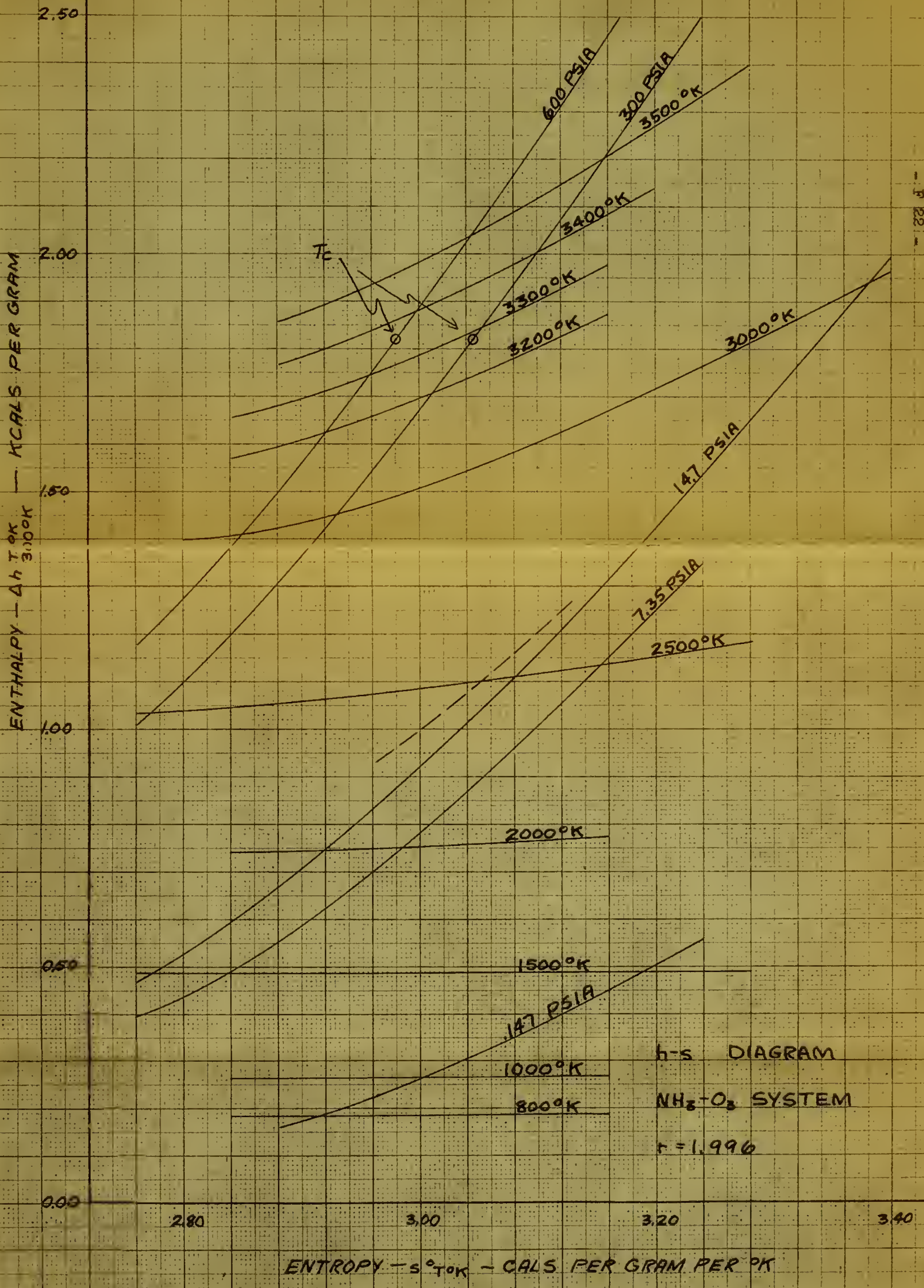
THEORETICAL SPECIFIC IMPULSE FROM h-s DIAGRAM

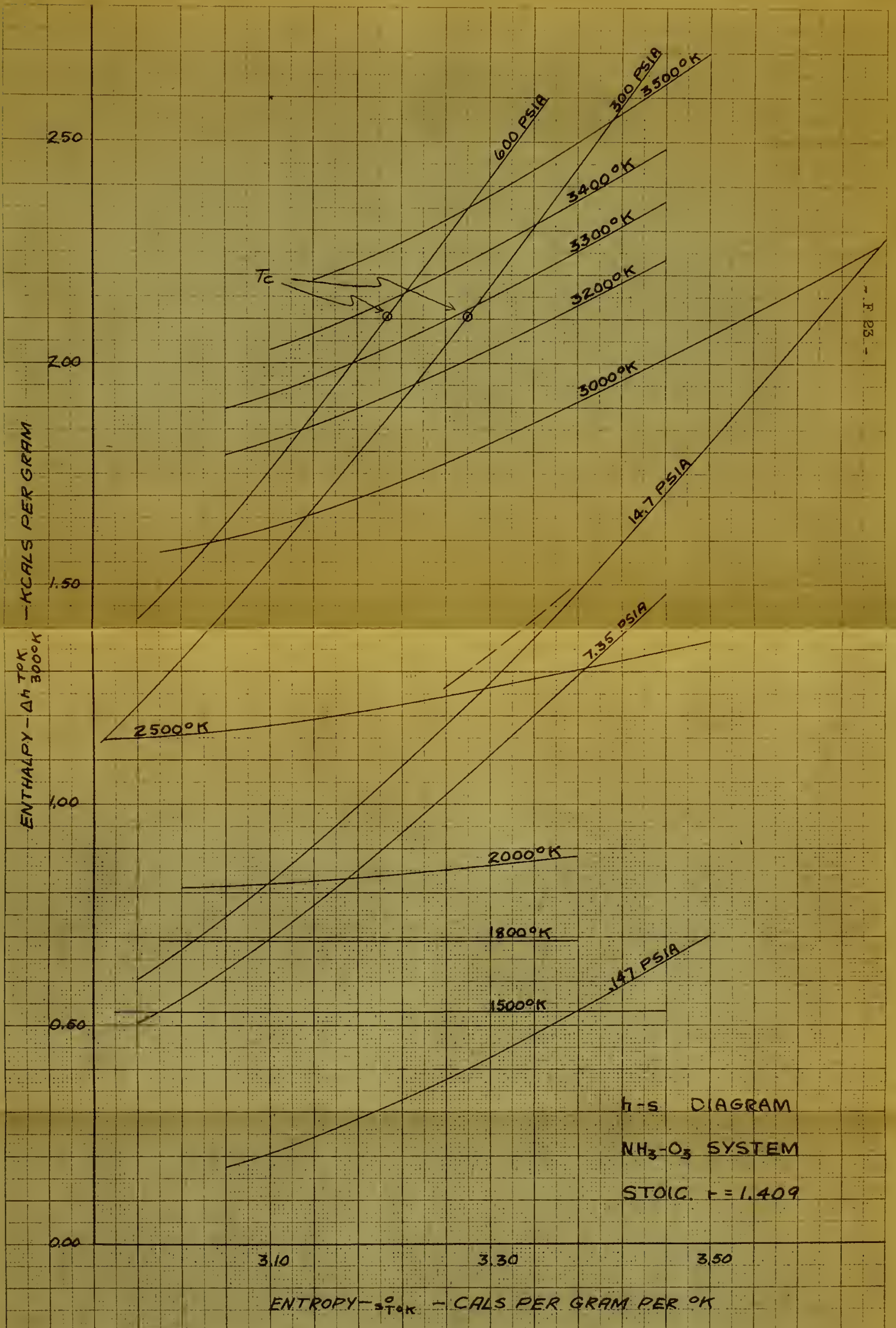


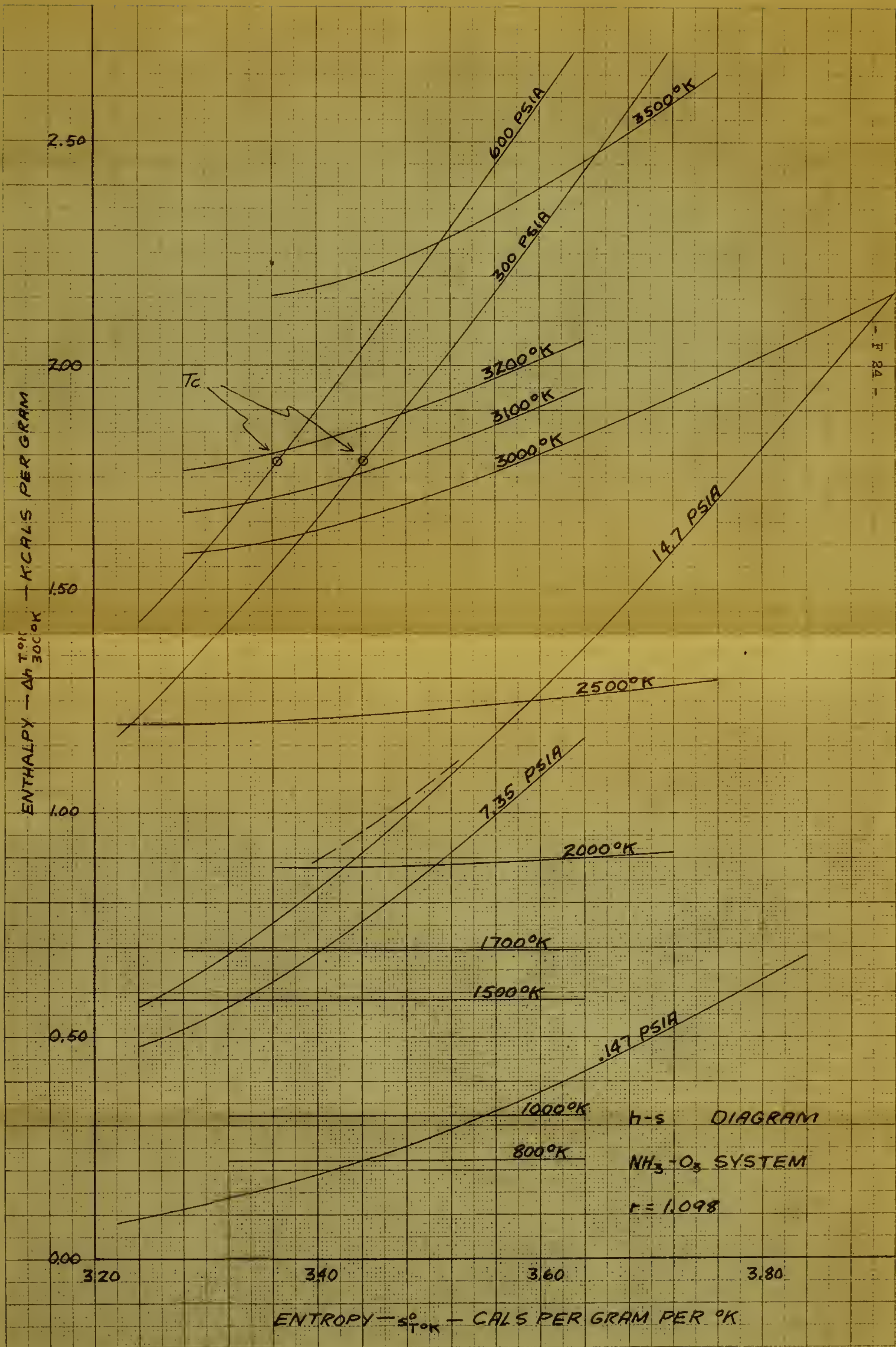


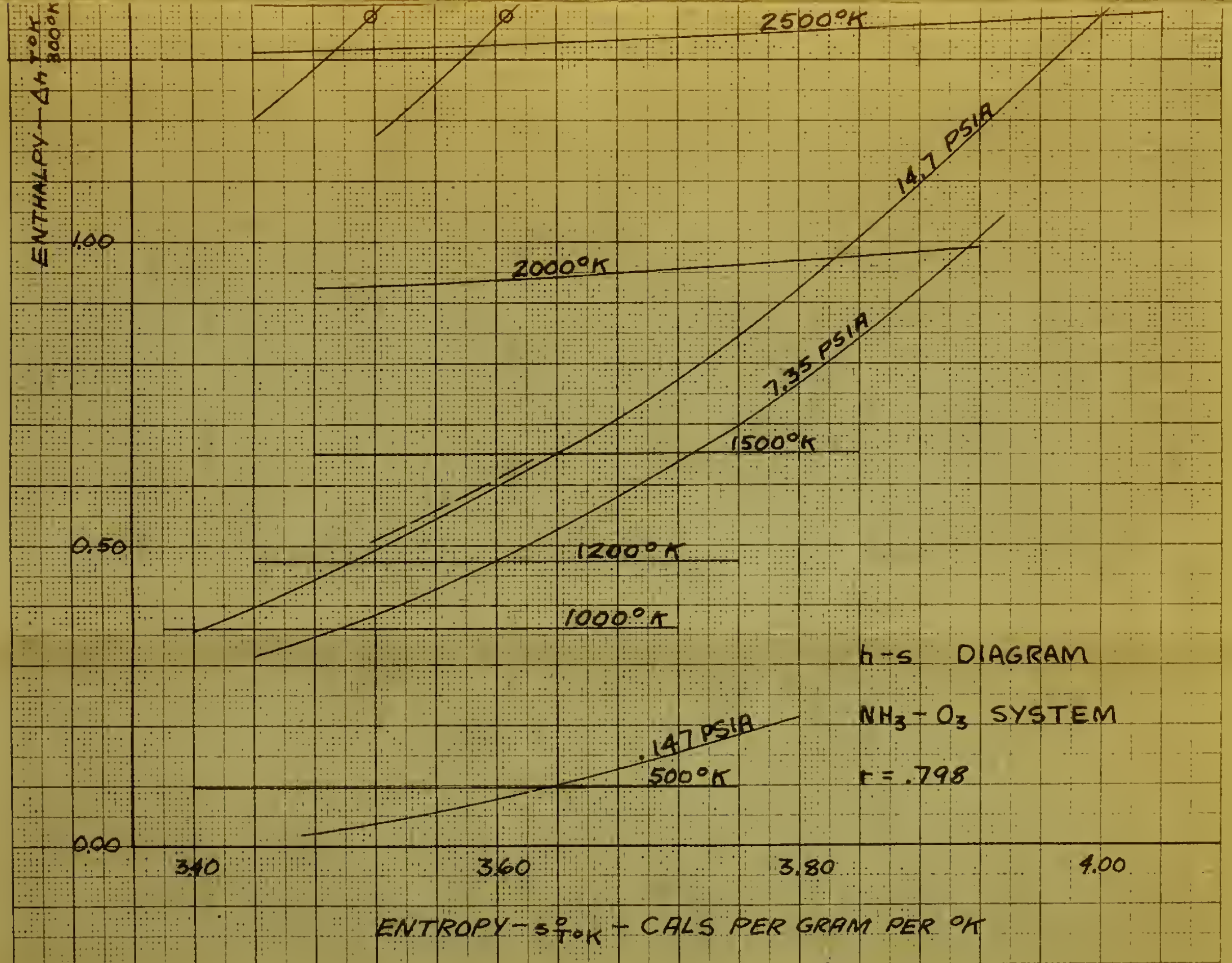
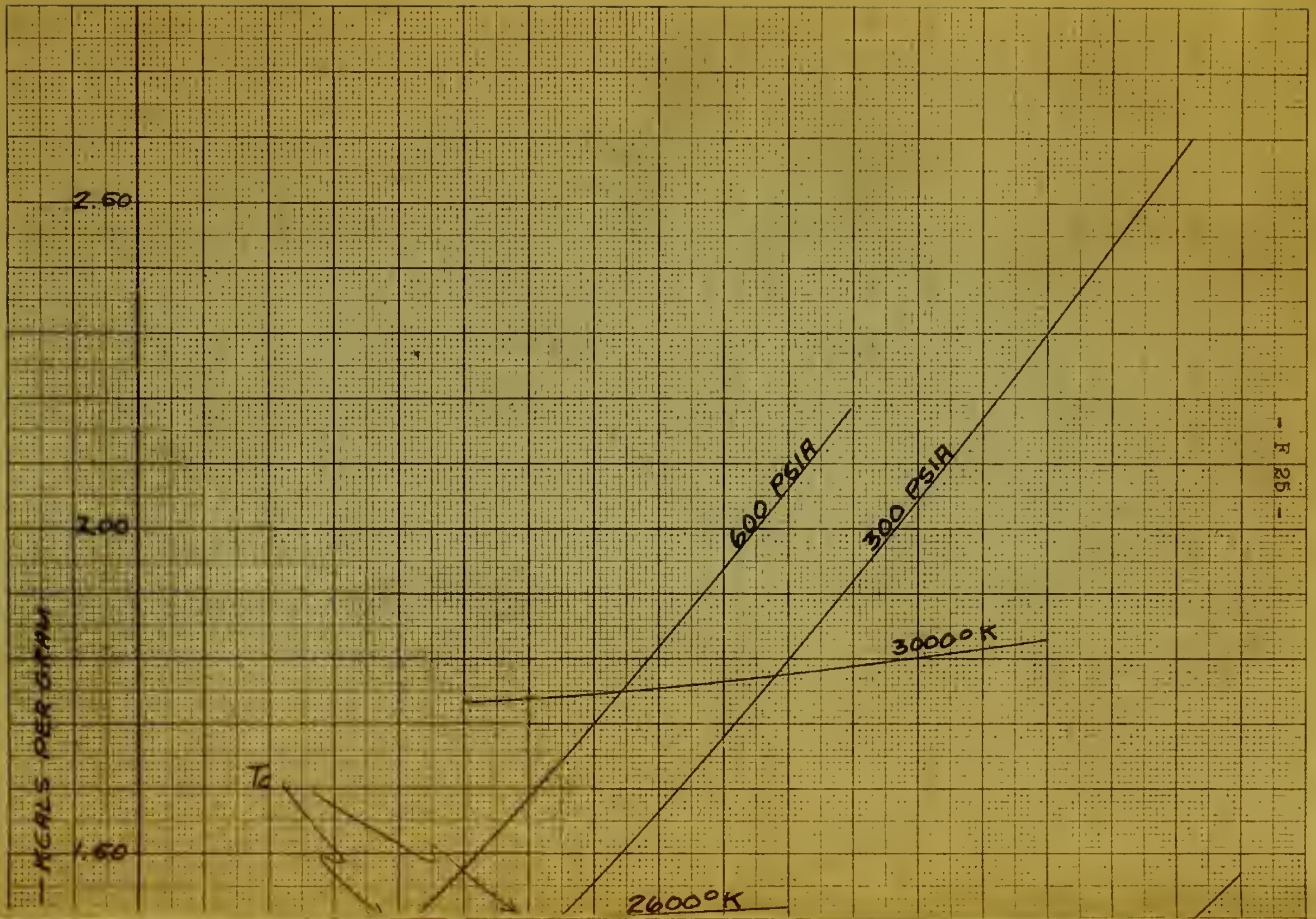


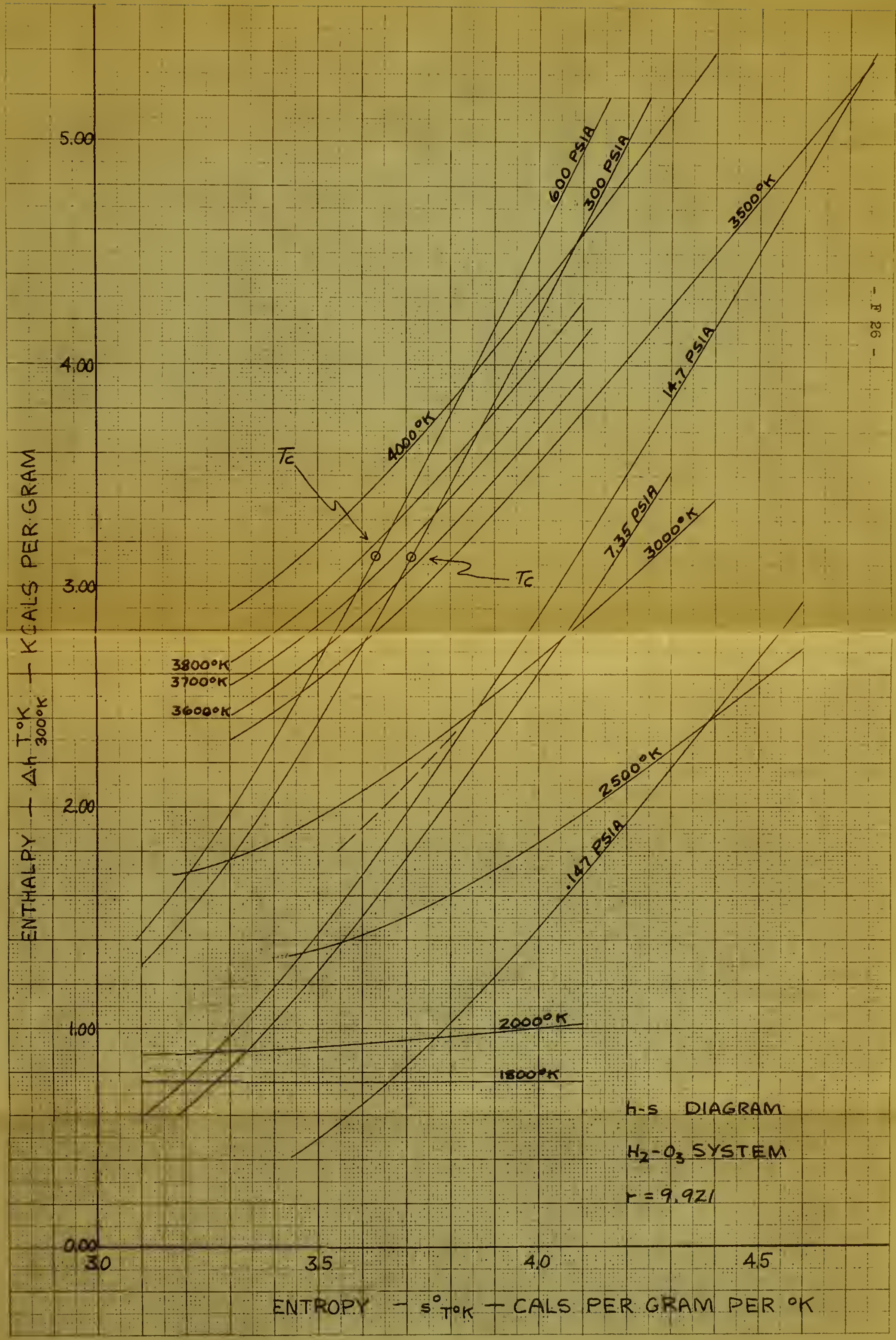


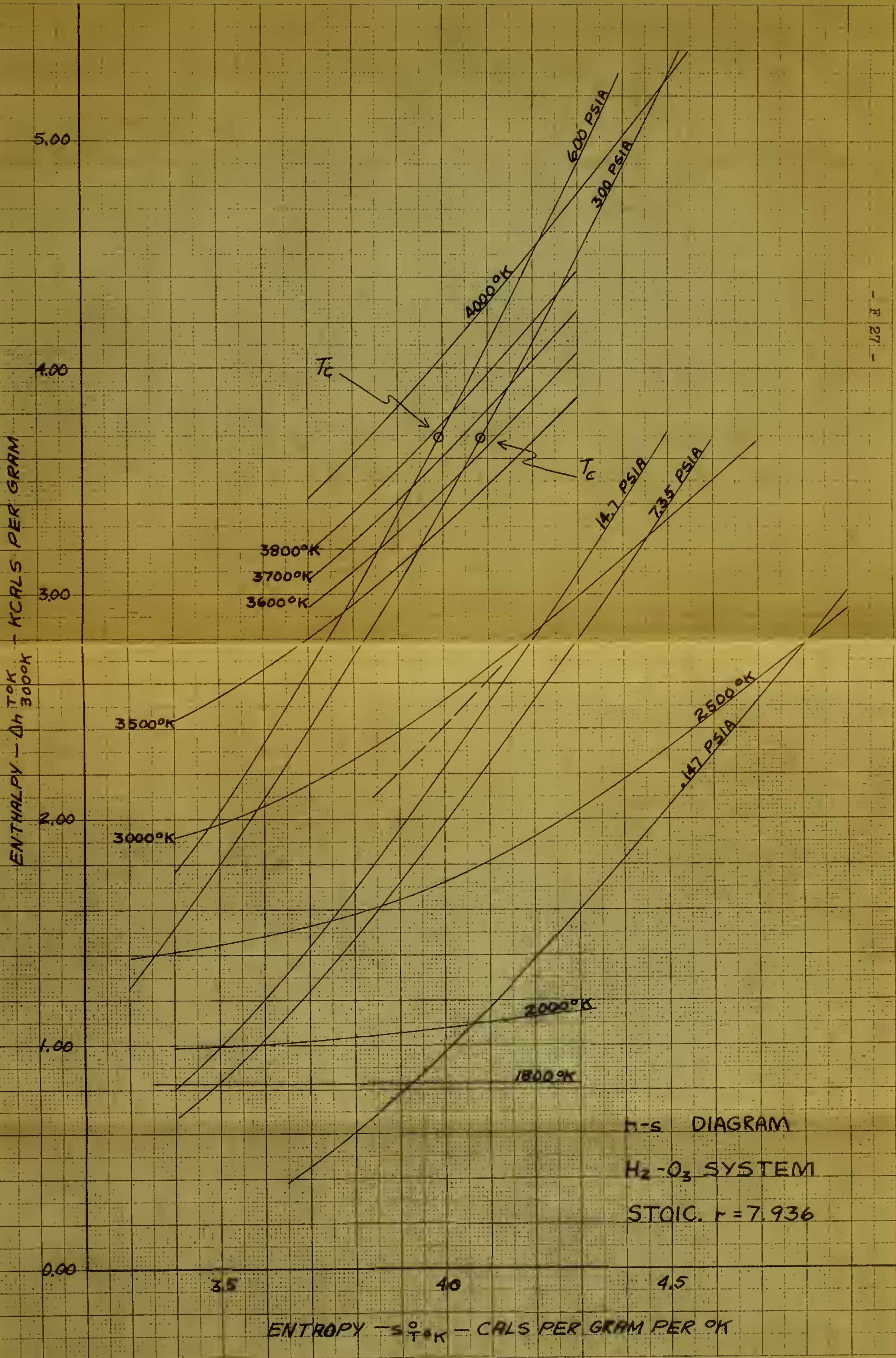


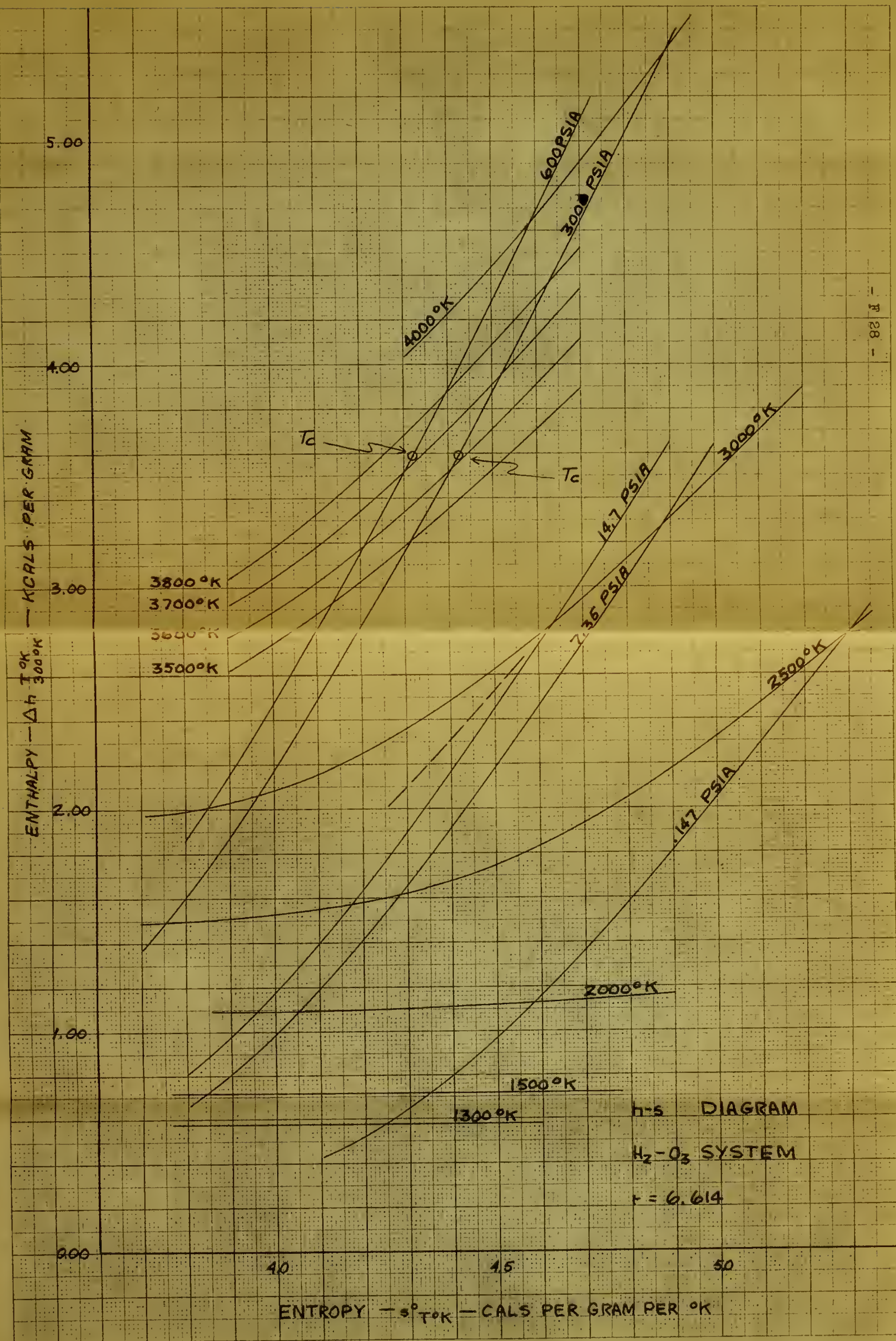


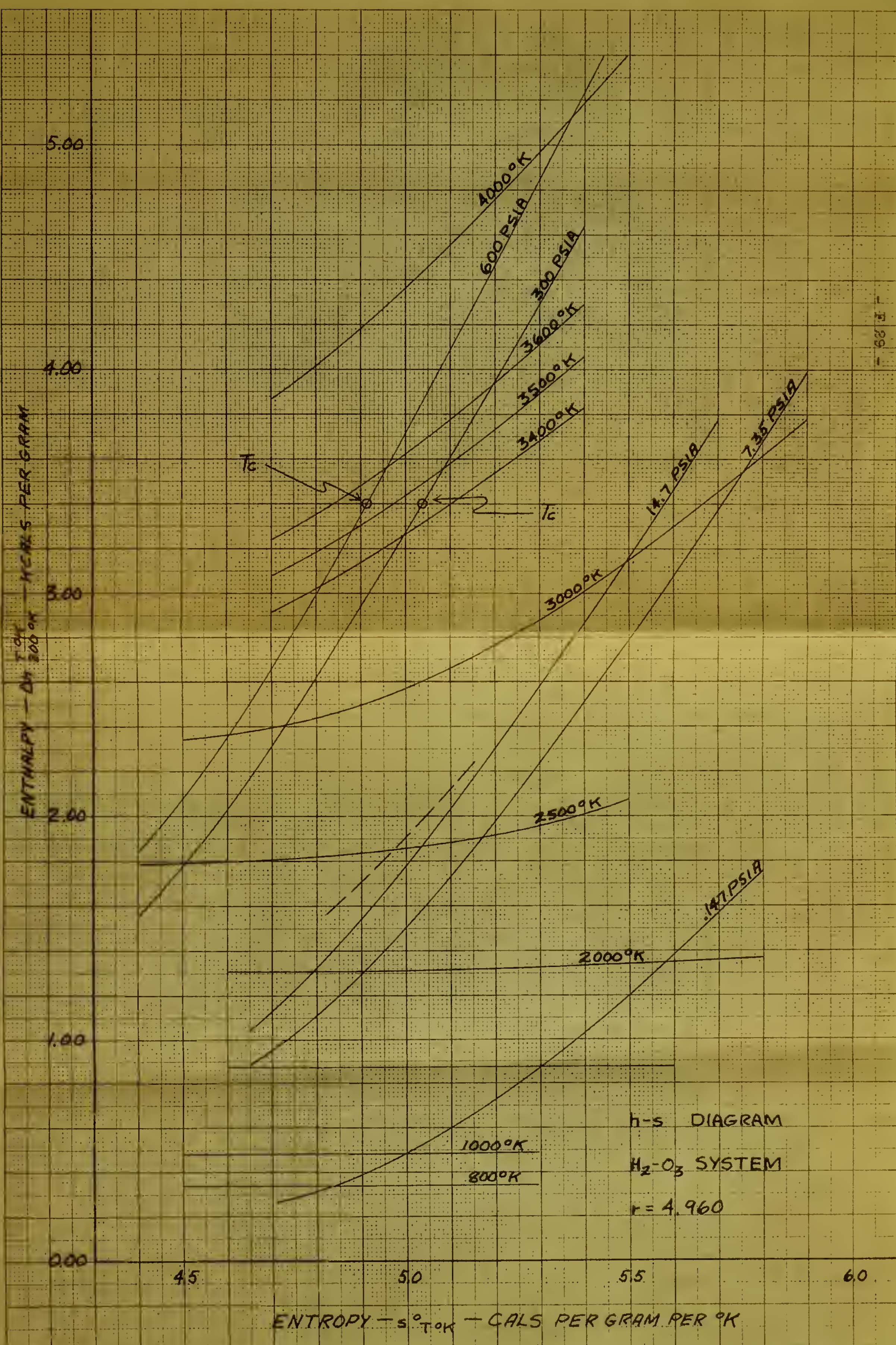












$h-s$ DIAGRAM

H_2-O_3 SYSTEM

$r = 4.960$

Fig. 28

Thesis

S57

Slater

AUTHOR

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AUTHOR		
enthalpy diagrams for rocket		
propellant systems		11

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